

# PATENT ABSTRACTS OF JAPAN

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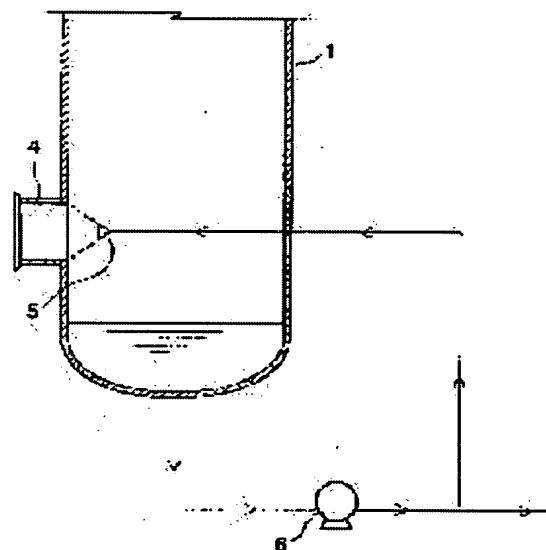
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## (54) METHOD FOR PREVENTING POLYMERIZATION OF EASILY POLYMERIZABLE COMPOUND

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method for preventing an easily polymerizable compound such as (meth)acrylic acid or (meth)acrylic ester(s) from polymerization tending to occur in its distillation unit during its distillation.

**SOLUTION:** This method for preventing an easily polymerizable compound from polymerization during distilling it using a distillation unit comprises feeding, by an atomizing charge means, a liquid substantially identical in composition with the liquid existing about the constitutive members to them arranged in the interior of the distillation unit; wherein the above liquid is set pref. at a temperature below that of the liquid existing about the constitutive members.



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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The polymerization prevention approach of the polymerizability compound characterized by supplying the liquid of the same presentation with a atomization injection means substantially with the liquid which exists in the perimeter of this configuration member to the configuration member which is the approach of distilling a polymerizability compound using a distillation apparatus, and was arranged in the interior of a distillation apparatus.

[Claim 2] The polymerization prevention approach according to claim 1 that the temperature of the liquid supplied with said atomization injection means is below the solution temperature around said configuration member.

[Claim 3] The polymerization prevention approach according to claim 1 or 2 which the liquid supplied with said atomization injection means is damp, and makes volume more than 0.5m<sup>3</sup>/m<sup>2</sup>Hr to the surface area of said configuration member.

[Claim 4] The polymerization prevention approach according to claim 1 to 3 that the liquid supplied with said atomization injection means contains polymerization inhibitor.

[Claim 5] The polymerization prevention approach according to claim 1 to 4 which supplies molecular oxygen content gas to said distillation apparatus.

[Claim 6] The polymerization prevention approach according to claim 1 to 5 that said configuration members are tray supporter material, packing supporter material, a flange, a nozzle, an end plate, a tower wall, a vapour chimney, a downcomer, a baffle, and a stirring shaft.

[Claim 7] The polymerization prevention approach according to claim 1 to 6 that said polymerizability compounds are an acrylic acid (meta) and/or (meta) acrylic ester.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the approach of preventing the polymerization at the time of distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta).

**[0002]**

**[Description of the Prior Art]** Distillation is actuation of condensing the steam which carries out the heating evaporation of the raw material liquid which consists of two or more sorts of liquid mixture with which the boiling points differ, and makes a low-boiling point component a subject, and performing segregation of liquid mixture, and separation of a component is easy for it when the difference in the relative volatility between components is great. However, since separation of a component cannot be performed by the concentration expected only by making some liquid evaporate and condense usual, it is common to distill a low-boiling point component from the overhead, and to take out a high-boiling component from a bottom by flowing back on the front face of a plate or packing from the overhead in a part of condensate, and contacting appropriately the steam which goes up a distillation apparatus, and the liquid which flows down from the overhead. In addition, as a distillation apparatus, there is a reactor equipped with the distilling column, and a film evaporator and a distilling column etc., and the capacitor, the reboiler, the heat tracing means, etc. are installed if needed. Moreover, in the case of a film evaporator, a column may be further installed in the upper part.

**[0003]** It is one example of the cross-section explanatory view of the plate type distillation apparatus 1 currently used widely by distillation of an acrylic acid (meta) or acrylic ester (meta) [it may be hereafter called an acrylic acid (meta) etc.], and drawing 1 makes the above-mentioned (meta) acrylic acid etc. a subject, it mentions as an example the case where the raw material liquid which contains an acetic acid as an impurity is used, and explains it. The above-mentioned raw material liquid is supplied into a distillation apparatus from a tower wall (L1). the acetic acid which is a low-boiling point component -- a column -- inner heating -- evaporating -- a column -- inside is gone up, and after being sent to a condenser 2 (L2) and being condensed from the overhead, it is taken out out of a system (L3). On the other hand, high-boiling point components, such as an acrylic acid (meta), are sent by degree process from a bottom (L4), and some purification liquid is returned to a distillation apparatus through a reboiler 3 (L5). in addition -- a purpose [ raise / since not only the acetic acid that is an impurity but the above-mentioned (meta) acrylic acid etc. is included in the condensate / the yield of an acrylic acid (meta) etc. ] -- carrying out -- the part -- reflux -- carrying out -- a column -- a bottom is made to flow down the above-mentioned (meta) acrylic acid etc. by being returned inside and carrying out a gas liquid contact again within (L6) and a distillation apparatus

**[0004]** Moreover, drawing 2 is an example of the explanatory view currently used widely by the reaction of acrylic ester (meta). an acrylic acid and the liquid containing alcohol being supplied to the reactor 18 (meta) which has ion exchange resin as a catalyst (L8), stirring with an agitator 21, and carrying out a steam injection at a reactor jacket -- (L9) -- generation water is driven out as vapor by distillation, making it react (L17). The esterified acrylic ester (meta) content liquid is extracted from (L15), and

sends the liquid to a purification process (L16). the distilling column which installed the vapor from a reactor 18 in the upper part -- supplying (L17) -- a column -- carrying out a gas liquid contact by the liquid supply (L10, L11) from the upper part, liquid, such as ester, an acrylic acid (meta), and alcohol, flows down to a reactor (L18). a column -- after the vapor from the upper part is sent to a condenser 24 (L12) and is condensed, it is sent to the oily water separation tub 23 (L13). The aqueous phase after oily water separation is discharged (L14), and an oil phase flows back to a distilling column 17 (L11). moreover, the need -- responding -- a column -- alcohol is supplied from the upper part -- it is constituted like (L10).

[0005] By the way, as for the above-mentioned (meta) acrylic acid etc., it is common to make the above-mentioned raw material liquid and reflux contain polymerization inhibitor, such as hydroquinone and phenothiazin, since it is the compound which is very easy to carry out a polymerization, and the approach of supplying molecular oxygen content gas from the lower part (L7) of a distillation apparatus further, and controlling a polymerization is also adopted.

[0006] Moreover, the method of preventing that a condensate carries out a polymerization in the condition that a steam condenses to JP,63-11921,B in a gaseous-phase section container wall etc., and there is no polymerization inhibitor in it as except these approaches by installing a heat tracing means (for example, heating jacket) in the evaporation side upper and lower sides of a distillation apparatus is indicated.

[0007] However, the polymerization was not necessarily prevented but suspending operation of a distillation apparatus and performing removal of a polymerization object according to generating of a polymerization, since purification effectiveness falls gradually was performed comparatively frequently.

[0008]

[Problem(s) to be Solved by the Invention] In being made paying attention to the above-mentioned situation, and distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta), this invention tends to offer the approach that the polymerization which is easy to generate inside a distillation apparatus can be prevented.

[0009]

[Means for Solving the Problem] The polymerization prevention approach of this invention which solved the above-mentioned technical problem is the approach of distilling a polymerizability compound using a distillation apparatus, and let it be a summary to supply the liquid of the same presentation with a atomization injection means substantially with the liquid which exists in the perimeter of this configuration member to the configuration member arranged in the interior of a distillation apparatus. In addition, as for the liquid supplied with said atomization injection means, it is desirable to carry out to below the solution temperature around the above-mentioned configuration member (or [ it is the same as the temperature of the liquid which exists in a perimeter ] or low). Moreover, it is desirable to get wet and to make volume (volume which adhered on the configuration member among those for the liquid atomized and supplied, and wet the configuration member) more than 0.5m<sup>3</sup>/m<sup>2</sup>Hr to the surface area of said configuration member, and, as for the liquid supplied with the above-mentioned atomization injection means, it is desirable to recommend to make polymerization inhibitor contain and to supply molecular oxygen content gas to the above-mentioned distillation apparatus further. In addition, air besides oxygen gas can be used as molecular oxygen content gas. It is desirable that it is 0.01 to 5 capacity [ of the amount of evaporation steams of the polymerizability compound which exists in a gaseous phase (reference condition conversion) ] %, and if the amount of supply (it is the amount of supply as oxygen gas when this gas contains components other than oxygen gas) of molecular oxygen content gas is 0.02 to 3 capacity %, it is more desirable.

[0010] As said configuration member, tray supporter material, packing supporter material, a flange, a nozzle, end plates (flat shape, a pan form, a half-ellipse form, a semi-sphere, cone bodily shape, etc.), a tower wall, a vapour chimney, a downcomer, a baffle, a stirring shaft, etc. are mentioned, and an acrylic acid (meta), acrylic ester (meta), etc. can be illustrated as said polymerizability compound.

[0011]

[Embodiment of the Invention] In case a polymerizability compound is distilled using a distillation

apparatus, a polymerization is carried out when a polymerizability compound stagnates on the configuration member front face inside a distillation apparatus (namely, thing which the same liquid stagnates in the same location). Since polymerization inhibitor stagnated as a liquid hardly contained when the liquid which the gaseous phase condensed especially stagnated on a configuration member, the amount of a polymerization object tended to increase and it had become the cause of making operation often stopping.

[0012] When this invention persons distilled polymerizability compounds, such as an acrylic acid, they hit on an idea of what is necessary being just to sprinkle using the liquid of the same presentation substantially with the liquid which can prevent the polymerization within a distillation apparatus effectively if it distills by [ as there being no stagnation of a liquid ] on the configuration member front face inside a distillation apparatus, continues all over a configuration member front face for that purpose, and exists in the perimeter of a configuration member to a header and this invention. It is desirable to make solution temperature of a spray the same as that of the temperature of the liquid which exists in the perimeter of a configuration member furthermore, or to make it low, and if polymerization inhibitor is made to contain further, it is desirable, and if molecular oxygen exists in a distillation apparatus, effectiveness is much more remarkable.

[0013] The liquid sprinkled to the configuration member in a distillation apparatus is the liquid of the same presentation as substantially as the liquid which exists in the perimeter of a configuration member. concrete -- feed liquid (raw material liquid) and a column -- what is necessary is just to sprinkle some or all of these liquids that what is necessary is just to use the extract liquid from inside, reflux, bottom circulation liquid (purification liquid), etc. Moreover, as for these liquid, it is more desirable than the liquid which exists in the perimeter of a configuration member that a polymerizability compound is low concentration or hypoviscosity, and diluting this liquid with water, alcohol, an azeotropy solvent, an extract solvent, etc. to extent which does not have a problem in the operation of distillation, and sprinkling by carrying out to it at lower concentration or viscosity is recommended.

[0014] Furthermore, since some supply liquid evaporates and spraying of liquid becomes unstable when the temperature of the liquid supplied to a configuration member is higher than the temperature around a configuration member, it is desirable to supply the liquid below the ambient temperature of the configuration member in a distillation apparatus. In addition, if the temperature of supply liquid is too low, since the gas of the perimeter of a configuration member will condense too much and the polymerization prevention effectiveness will decrease, as for whenever [ supply solution temperature ], it is more desirable than the ambient temperature of the configuration member in a distillation apparatus to make it low 0-40 degrees C, and if it is 1-30 degrees C or less, it is more desirable.

[0015] What is necessary is to know hydroquinone, phenothiazin, METOKINON, manganese acetate, nitrosophenol, a cupferron, N-oxy compound, dibutyl thio carbamic acid copper, etc., to make it dissolve in a polymerizability compound, a solvent, etc., and to throw the above-mentioned polymerization inhibitor into the supply line of feed liquid, or reflux and bottom circulation liquid as polymerization inhibitor, or just to supply in a direct distillation apparatus. In addition, what is necessary is to return in a distillation apparatus and just to sprinkle to a configuration member, even if it does not newly add polymerization inhibitor since the polymerization inhibitor fed into the distillation apparatus usually contains comparatively so much in bottom circulation liquid.

[0016] When preventing a polymerization, supplying molecular oxygen content gas is recommended. The above-mentioned molecular oxygen content gas If an oxygen density is low, while the amount of molecule-like oxygen gas required for polymerization prevention will increase and the capacity in vacuum devices will become large Since the amount of the polymerization object in a distillation apparatus and vacuum devices increases, it is desirable that it is more than the oxygen density (20 - 21vol%) of air, and if it is 40 - 100vol%, it is more desirable, and if it is 80 - 100vol%, it is much more desirable.

[0017] Liquid is sprinkled with a atomization injection means (spray) so that the whole surface may be soaked in homogeneity to the configuration member in a distillation apparatus by this invention approach, but although what is necessary is just to set up suitably the conditions of atomization, such as

a type of a spray, and the number of nozzles, a flow rate, according to the ambient atmosphere in the arrangement location of a configuration member, and a distillation apparatus, it is desirable to set up so that the whole surface of a configuration member may be soaked anyway in homogeneity as much as possible.

[0018] Moreover, spraying volume gets wet to configuration member surface area, if volume is more than 0.5m<sup>3</sup>/m<sup>2</sup>Hr, it is desirable, if it is more than 1m<sup>3</sup>/m<sup>2</sup>Hr, it is more desirable, and if it is more than 2m<sup>3</sup>/m<sup>2</sup>Hr, it is much more desirable. In addition, the above-mentioned configuration member surface area is an area expressed with  $D(\pi/4)^2$  (however, D diameter) about a flange or a nozzle, and a wetted area computable in the distance of whenever [ angle-of-divergence / of a liquid spraying nozzle ], and a configuration member front face is said about other members.

[0019] As a configuration member currently arranged in the distillation apparatus, there are tray supporter material, packing supporter material, a flange, a nozzle, an end plate, a tower wall, a vapour chimney, a downcomer, a baffle, a stirring shaft, etc. In addition, by this invention, including all the things currently installed in the distillation apparatus, the inlet port or outlet nozzle of gas or liquid is begun, and a manhole, instruments seats (a pressure gage seat, a liquid level connection, temperature connection, etc.), etc. are mentioned with a nozzle. It is such a configuration member and polymerization generating can be prevented by carrying out the spray of the liquid to the part which the liquid generated by condensation of a gaseous phase stagnates, and a polymerization tends to generate, and preventing stagnation of liquid. Moreover, a polymerization can be prevented by moving the liquid which has stagnated with spray liquid also about the liquid phase section.

[0020] As a suitable example of the polymerizability compound concerning this invention An acrylic acid and acrylic ester (meta) are mentioned. (Meta) As a latter example Methyl ester, ethyl ester, isopropyl ester, Although n-propyl ester, isobutyl ester, n-butylester, 2-ethylhexyl ester, 2-hydroxyethyl ester, hydroxy propyl ester, dialkyl aminoethyl ester, etc. are mentioned this invention approach is very effective to the acrylic acid which is easy to carry out a polymerization most easily especially (meta).

[0021] Each drawing 3 -8 is the approximate account Fig. showing the example of this invention, and drawing 3 returns the purification liquid drawn from the bottom to a distillation apparatus 1 to the manhole 4 established in the lower part of a distillation apparatus 1, and shows how to carry out a spray with the atomization injection means 5. Drawing 4 shows how to carry out the spray of the reflux with a atomization injection means 9 to have an exhaust nozzle in four places to the end plate 7 arranged in the overhead, and/or the vapor line 8 from the overhead to the condenser of degree process. Drawing 5 shows how to throw in raw material liquid to downcomer 10a of the tray 10 lower part of a plate type distillation apparatus. To the vapour chimney 11 arranged in order to extract liquid from the middle in a distillation apparatus, drawing 6 returns some extract liquid and shows how to carry out a spray with the atomization injection means 12. Drawing 7 shows how to carry out the spray of the liquid with the atomization injection means 17 to the supporter material 16 of a packed bed 15 in the restoration type distillation apparatus 14. Drawing 8 shows how to carry out a spray with the atomization injection means 25 to the agitator 21, the baffle 20, and the manhole 26 in the reactor which carries out reaction distillation. Moreover, by fall to the liquid phase section of not only the polymerization of the liquid which the gaseous phase of the gaseous-phase section condensed but spray liquid, drawing 3 -8 make migration of liquid cause, they lessen the residence time, and also show the example which prevents a polymerization.

[0022] Hereafter, although an example explains this invention to a detail further, the following example is not the thing of the property which limits this invention, and each thing done for a design change based on before and the after-mentioned main point is included in the technical range of this invention.

[0023]  
[Example] The acrylic acid was refined using the distillation apparatus made from stainless steel (SUS316) which carried out the interior of the sheave tray made from stainless steel (SUS316) of the [example 1] bore of 1300mm, and 50 steps of number of stageses. Overhead temperature under distillation was set into 63 degrees C, the pressure was set to 4.7kPa(s) (35mmHg), the temperature of a bottom was set as 100 degrees C, and the reflux ratio was set as 1.8. Raw material liquid was made to

contain 50 ppm of phenothiazins as a polymerization inhibitor, and reflux was made to contain 100 ppm of METOKINON. Furthermore, continuous running of the molecular oxygen was supplied and carried out from the bottom under the conditions of 0.3vol(s).% to the amount of overhead vapor (reference condition conversion).

[0024] When 90-degree C liquid was sprinkled in the manhole (path 500mmphi) of a bottom on the whole surface using bottom circulation liquid by the spray of the flow rate (getting wet 2.5m<sup>3</sup>/m<sup>2</sup> of volume Hr) of 500l. / hr at that time, it was able to operate favorably for about one month.

[0025] It distilled like the example except having not performed a spray in the manhole of the [example 1 of comparison] bottom. Consequently, after working for eight days, the liquid draw became impossible from the bottom. It stops, and when checked, about 2kg polymerization object had adhered to the bottom section, and it was blocking extract piping of the bottom section.

[0026] In the [example 2] example 1, it distilled like the example 1 except having not supplied molecular oxygen to a bottom. Consequently, after working for 17 days, the draw of liquid became impossible from the bottom. It stops, and when checked, about 1kg polymerization object adhered to the bottom section, and it was blocking draw piping of the bottom section. Although days of operation are twice [ more than ] the example of a comparison, it turns out that it is desirable to supply molecular oxygen.

[0027] In the [example 3] example 1, it distilled like the example 1 except having made temperature of the liquid of a spray into 55 degrees C, and having sprinkled it. Consequently, since the polymerization object was checked by the extract liquid after operation on the 25th, when it stopped and checked, about 0.5kg polymerization object had adhered to the bottom section.

[0028] Esterification reaction distillation of 2-ethylhexyl alcohol and an acrylic acid was performed using the stirred-tank-type reactor with a [example 4] bore [ of 3500mm ], and a body height of 3500mm made from stainless steel (SUS316), and the packed column with a bore [ of 1100mm ] installed in the upper part, and a restoration height (packing: cascade mini Ring 2 P) of 5000mm made from stainless steel (SUS316). the column top temperature under reaction distillation -- 43 degrees C and a pressure -- the reaction temperature of 8kPa(s) (absolute pressure) and a reactor -- 90 degrees C -- carrying out -- as a catalyst -- ion-exchange resin -- using -- a column -- phenothiazin 100ppm from the upper part -- from the contained 2-ethylhexyl alcohol and the reactor upper part, the acrylic-acid content liquid containing 200 ppm of METOKINON was supplied. Furthermore, continuous running of the air was supplied and carried out from the reactor lower part under the conditions of 0.15vol(s).% to the amount of overhead vapor (reference condition conversion).

[0029] a part of reaction mixture extracted from the reactor at that time -- using -- two baffles (path 200mmphi) -- respectively -- 500l. / hr (getting wet -- volume --) When it sprinkled in 1.6m<sup>3</sup>/m<sup>2</sup>hr and an up manhole (path 500mmphi) with die length of 500mm which gets wet by the spray of 500l. / hr (it gets wet and is 1.6m<sup>3</sup>/m<sup>2</sup>hr at volume and die length of 500mm which gets wet), it was able to operate favorably for about one month.

[0030] Reaction distillation was performed like the example 3 except having not performed the [example 2 of comparison] spray. Consequently, since the polymerization object was seen by reaction draw liquid after operation on the 20th, when it stopped and checked, about 2kg polymerization object had adhered to the baffle, the agitator, and the manhole.

[0031]

[Effect of the Invention] In distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta), since this invention is constituted as mentioned above, the approach of preventing a polymerization can be offered.

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the approach of preventing the polymerization at the time of distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta).

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PRIOR ART

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[Description of the Prior Art] Distillation is actuation of condensing the steam which carries out the heating evaporation of the raw material liquid which consists of two or more sorts of liquid mixture with which the boiling points differ, and makes a low-boiling point component a subject, and performing segregation of liquid mixture, and separation of a component is easy for it when the difference in the relative volatility between components is great. However, since separation of a component cannot be performed by the concentration expected only by making some liquid evaporate and condense usual, it is common to distill a low-boiling point component from the overhead, and to take out a high-boiling component from a bottom by flowing back on the front face of a plate or packing from the overhead in a part of condensate, and contacting appropriately the steam which goes up a distillation apparatus, and the liquid which flows down from the overhead. In addition, as a distillation apparatus, there is a reactor equipped with the distilling column, and a film evaporator and a distilling column etc., and the capacitor, the reboiler, the heat tracing means, etc. are installed if needed. Moreover, in the case of a film evaporator, a column may be further installed in the upper part.

[0003] It is one example of the cross-section explanatory view of the plate type distillation apparatus 1 currently used widely by distillation of an acrylic acid (meta) or acrylic ester (meta) [it may be hereafter called an acrylic acid (meta) etc.], and drawing 1 makes the above-mentioned (meta) acrylic acid etc. a subject, it mentions as an example the case where the raw material liquid which contains an acetic acid as an impurity is used, and explains it. The above-mentioned raw material liquid is supplied into a distillation apparatus from a tower wall (L1). the acetic acid which is a low-boiling point component -- a column -- inner heating -- evaporating -- a column -- inside is gone up, and after being sent to a condenser 2 (L2) and being condensed from the overhead, it is taken out out of a system (L3). On the other hand, high-boiling point components, such as an acrylic acid (meta), are sent by degree process from a bottom (L4), and some purification liquid is returned to a distillation apparatus through a reboiler 3 (L5). in addition -- a purpose [ raise / since not only the acetic acid that is an impurity but the above-mentioned (meta) acrylic acid etc. is included in the condensate / the yield of an acrylic acid (meta) etc. ] -- carrying out -- the part -- reflux -- carrying out -- a column -- a bottom is made to flow down the above-mentioned (meta) acrylic acid etc. by being returned inside and carrying out a gas liquid contact again within (L6) and a distillation apparatus

[0004] Moreover, drawing 2 is an example of the explanatory view currently used widely by the reaction of acrylic ester (meta). an acrylic acid and the liquid containing alcohol being supplied to the reactor 18 (meta) which has ion exchange resin as a catalyst (L8), stirring with an agitator 21, and carrying out a steam injection at a reactor jacket -- (L9) -- generation water is driven out as vapor by distillation, making it react (L17). The esterified acrylic ester (meta) content liquid is extracted from (L15), and sends the liquid to a purification process (L16). the distilling column which installed the vapor from a reactor 18 in the upper part -- supplying (L17) -- a column -- carrying out a gas liquid contact by the liquid supply (L10, L11) from the upper part, liquid, such as ester, an acrylic acid (meta), and alcohol, flows down to a reactor (L18). a column -- after the vapor from the upper part is sent to a condenser 24 (L12) and is condensed, it is sent to the oily water separation tub 23 (L13). The aqueous phase after oily

water separation is discharged (L14), and an oil phase flows back to a distilling column 17 (L11). moreover, the need -- responding -- a column -- alcohol is supplied from the upper part -- it is constituted like (L10).

[0005] By the way, as for the above-mentioned (meta) acrylic acid etc., it is common to make the above-mentioned raw material liquid and reflux contain polymerization inhibitor, such as hydroquinone and phenothiazin, since it is the compound which is very easy to carry out a polymerization, and the approach of supplying molecular oxygen content gas from the lower part (L7) of a distillation apparatus further, and controlling a polymerization is also adopted.

[0006] Moreover, the method of preventing that a condensate carries out a polymerization in the condition that a steam condenses to JP,63-11921,B in a gaseous-phase section container wall etc., and there is no polymerization inhibitor in it as except these approaches by installing a heat tracing means (for example, heating jacket) in the evaporation side upper and lower sides of a distillation apparatus is indicated.

[0007] However, the polymerization was not necessarily prevented but suspending operation of a distillation apparatus and performing removal of a polymerization object according to generating of a polymerization, since purification effectiveness falls gradually was performed comparatively frequently.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] In distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta), since this invention is constituted as mentioned above, the approach of preventing a polymerization can be offered.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] In being made paying attention to the above-mentioned situation, and distilling polymerizability compounds, such as an acrylic acid (meta) and acrylic ester (meta), this invention tends to offer the approach that the polymerization which is easy to generate inside a distillation apparatus can be prevented.

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**MEANS**

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[Means for Solving the Problem] The polymerization prevention approach of this invention which solved the above-mentioned technical problem is the approach of distilling a polymerizability compound using a distillation apparatus, and let it be a summary to supply the liquid of the same presentation with a atomization injection means substantially with the liquid which exists in the perimeter of this configuration member to the configuration member arranged in the interior of a distillation apparatus. In addition, as for the liquid supplied with said atomization injection means, it is desirable to carry out to below the solution temperature around the above-mentioned configuration member (or [ it is the same as the temperature of the liquid which exists in a perimeter ] or low). Moreover, it is desirable to get wet and to make volume (volume which adhered on the configuration member among those for the liquid atomized and supplied, and wet the configuration member) more than 0.5m<sup>3</sup>/m<sup>2</sup>Hr to the surface area of said configuration member, and, as for the liquid supplied with the above-mentioned atomization injection means, it is desirable to recommend to make polymerization inhibitor contain and to supply molecular oxygen content gas to the above-mentioned distillation apparatus further. In addition, air besides oxygen gas can be used as molecular oxygen content gas. It is desirable that it is 0.01 to 5 capacity [ of the amount of evaporation steams of the polymerizability compound which exists in a gaseous phase (reference condition conversion) ] %, and if the amount of supply (it is the amount of supply as oxygen gas when this gas contains components other than oxygen gas) of molecular oxygen content gas is 0.02 to 3 capacity %, it is more desirable.

[0010] As said configuration member, tray supporter material, packing supporter material, a flange, a nozzle, end plates (flat shape, a pan form, a half-ellipse form, a semi-sphere, cone bodily shape, etc.), a tower wall, a vapour chimney, a downcomer, a baffle, a stirring shaft, etc. are mentioned, and an acrylic acid (meta), acrylic ester (meta), etc. can be illustrated as said polymerizability compound.

[0011]  
[Embodiment of the Invention] In case a polymerizability compound is distilled using a distillation apparatus, a polymerization is carried out when a polymerizability compound stagnates on the configuration member front face inside a distillation apparatus (namely, thing which the same liquid stagnates in the same location). Since polymerization inhibitor stagnated as a liquid hardly contained when the liquid which the gaseous phase condensed especially stagnated on a configuration member, the amount of a polymerization object tended to increase and it had become the cause of making operation often stopping.

[0012] When this invention persons distilled polymerizability compounds, such as an acrylic acid, they hit on an idea of what is necessary being just to sprinkle using the liquid of the same presentation substantially with the liquid which can prevent the polymerization within a distillation apparatus effectively if it distills by [ as there being no stagnation of a liquid ] on the configuration member front face inside a distillation apparatus, continues all over a configuration member front face for that purpose, and exists in the perimeter of a configuration member to a header and this invention. It is desirable to make solution temperature of a spray the same as that of the temperature of the liquid which exists in the perimeter of a configuration member furthermore, or to make it low, and if polymerization inhibitor is

made to contain further, it is desirable, and if molecular oxygen exists in a distillation apparatus, effectiveness is much more remarkable.

[0013] The liquid sprinkled to the configuration member in a distillation apparatus is the liquid of the same presentation as substantially as the liquid which exists in the perimeter of a configuration member. concrete -- feed liquid (raw material liquid) and a column -- what is necessary is just to sprinkle some or all of these liquids that what is necessary is just to use the extract liquid from inside, reflux, bottom circulation liquid (purification liquid), etc. Moreover, as for these liquid, it is more desirable than the liquid which exists in the perimeter of a configuration member that a polymerizability compound is low concentration or hypoviscosity, and diluting this liquid with water, alcohol, an azeotropy solvent, an extract solvent, etc. to extent which does not have a problem in the operation of distillation, and sprinkling by carrying out to it at lower concentration or viscosity is recommended.

[0014] Furthermore, since some supply liquid evaporates and spraying of liquid becomes unstable when the temperature of the liquid supplied to a configuration member is higher than the temperature around a configuration member, it is desirable to supply the liquid below the ambient temperature of the configuration member in a distillation apparatus. In addition, if the temperature of supply liquid is too low, since the gas of the perimeter of a configuration member will condense too much and the polymerization prevention effectiveness will decrease, as for whenever [ supply solution temperature ], it is more desirable than the ambient temperature of the configuration member in a distillation apparatus to make it low 0-40 degrees C, and if it is 1-30 degrees C or less, it is more desirable.

[0015] What is necessary is to know hydroquinone, phenothiazin, METOKINON, manganese acetate, nitrosophenol, a cupferron, N-oxyl compound, dibutyl thio carbamic acid copper, etc., to make it dissolve in a polymerizability compound, a solvent, etc., and to throw the above-mentioned polymerization inhibitor into the supply line of feed liquid, or reflux and bottom circulation liquid as polymerization inhibitor, or just to supply in a direct distillation apparatus. In addition, what is necessary is to return in a distillation apparatus and just to sprinkle to a configuration member, even if it does not newly add polymerization inhibitor since the polymerization inhibitor fed into the distillation apparatus usually contains comparatively so much in bottom circulation liquid.

[0016] When preventing a polymerization, supplying molecular oxygen content gas is recommended. The above-mentioned molecular oxygen content gas If an oxygen density is low, while the amount of molecule-like oxygen gas required for polymerization prevention will increase and the capacity in vacuum devices will become large Since the amount of the polymerization object in a distillation apparatus and vacuum devices increases, it is desirable that it is more than the oxygen density (20 - 21vol%) of air, and if it is 40 - 100vol%, it is more desirable, and if it is 80 - 100vol%, it is much more desirable.

[0017] Liquid is sprinkled with a atomization injection means (spray) so that the whole surface may be soaked in homogeneity to the configuration member in a distillation apparatus by this invention approach, but although what is necessary is just to set up suitably the conditions of atomization, such as a type of a spray, and the number of nozzles, a flow rate, according to the ambient atmosphere in the arrangement location of a configuration member, and a distillation apparatus, it is desirable to set up so that the whole surface of a configuration member may be soaked anyway in homogeneity as much as possible.

[0018] Moreover, spraying volume gets wet to configuration member surface area, if volume is more than 0.5m<sup>3</sup>/m<sup>2</sup>Hr, it is desirable, if it is more than 1m<sup>3</sup>/m<sup>2</sup>Hr, it is more desirable, and if it is more than 2m<sup>3</sup>/m<sup>2</sup>Hr, it is much more desirable. In addition, the above-mentioned configuration member surface area is an area expressed with  $D(\pi/4)^2$  (however, D diameter) about a flange or a nozzle, and a wetted area computable in the distance of whenever [ angle-of-divergence / of a liquid spraying nozzle ], and a configuration member front face is said about other members.

[0019] As a configuration member currently arranged in the distillation apparatus, there are tray supporter material, packing supporter material, a flange, a nozzle, an end plate, a tower wall, a vapour chimney, a downcomer, a baffle, a stirring shaft, etc. In addition, by this invention, including all the things currently installed in the distillation apparatus, the inlet port or outlet nozzle of gas or liquid is

begun, and a manhole, instruments seats (a pressure gage seat, a liquid level connection, temperature connection, etc.), etc. are mentioned with a nozzle. It is such a configuration member and polymerization generating can be prevented by carrying out the spray of the liquid to the part which the liquid generated by condensation of a gaseous phase stagnates, and a polymerization tends to generate, and preventing stagnation of liquid. Moreover, a polymerization can be prevented by moving the liquid which has stagnated with spray liquid also about the liquid phase section.

[0020] As a suitable example of the polymerizability compound concerning this invention An acrylic acid and acrylic ester (meta) are mentioned. (Meta) As a latter example Methyl ester, ethyl ester, isopropyl ester, Although n-propyl ester, isobutyl ester, n-butylester, 2-ethylhexyl ester, 2-hydroxyethyl ester, hydroxy propyl ester, dialkyl aminoethyl ester, etc. are mentioned this invention approach is very effective to the acrylic acid which is easy to carry out a polymerization most easily especially (meta).

[0021] Each drawing 3 -8 is the approximate account Fig. showing the example of this invention, and drawing 3 returns the purification liquid drawn from the bottom to a distillation apparatus 1 to the manhole 4 established in the lower part of a distillation apparatus 1, and shows how to carry out a spray with the atomization injection means 5. Drawing 4 shows how to carry out the spray of the reflux with a atomization injection means 9 to have an exhaust nozzle in four places to the end plate 7 arranged in the overhead, and/or the vapor line 8 from the overhead to the condenser of degree process. Drawing 5 shows how to throw in raw material liquid to downcomer 10a of the tray 10 lower part of a plate type distillation apparatus. To the vapour chimney 11 arranged in order to extract liquid from the middle in a distillation apparatus, drawing 6 returns some extract liquid and shows how to carry out a spray with the atomization injection means 12. Drawing 7 shows how to carry out the spray of the liquid with the atomization injection means 17 to the supporter material 16 of a packed bed 15 in the restoration type distillation apparatus 14. Drawing 8 shows how to carry out a spray with the atomization injection means 25 to the agitator 21, the baffle 20, and the manhole 26 in the reactor which carries out reaction distillation. Moreover, by fall to the liquid phase section of not only the polymerization of the liquid which the gaseous phase of the gaseous-phase section condensed but spray liquid, drawing 3 -8 make migration of liquid cause, they lessen the residence time, and also show the example which prevents a polymerization.

[0022] Hereafter, although an example explains this invention to a detail further, the following example is not the thing of the property which limits this invention, and each thing done for a design change based on before and the after-mentioned main point is included in the technical range of this invention.

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[Translation done.]



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**EXAMPLE**

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[Example] The acrylic acid was refined using the distillation apparatus made from stainless steel (SUS316) which carried out the interior of the sheave tray made from stainless steel (SUS316) of the [example 1] bore of 1300mm, and 50 steps of number of stageses. Overhead temperature under distillation was set into 63 degrees C, the pressure was set to 4.7kPa(s) (35mmHg), the temperature of a bottom was set as 100 degrees C, and the reflux ratio was set as 1.8. Raw material liquid was made to contain 50 ppm of phenothiazins as a polymerization inhibitor, and reflux was made to contain 100 ppm of METOKINON. Furthermore, continuous running of the molecular oxygen was supplied and carried out from the bottom under the conditions of 0.3vol(s).% to the amount of overhead vapor (reference condition conversion).

[0024] When 90-degree C liquid was sprinkled in the manhole (path 500mmphi) of a bottom on the whole surface using bottom circulation liquid by the spray of the flow rate (getting wet 2.5m3/m2 of volume Hr) of 500l. / hr at that time, it was able to operate favorably for about one month.

[0025] It distilled like the example except having not performed a spray in the manhole of the [example 1 of comparison] bottom. Consequently, after working for eight days, the liquid draw became impossible from the bottom. It stops, and when checked, about 2kg polymerization object had adhered to the bottom section, and it was blocking extract piping of the bottom section.

[0026] In the [example 2] example 1, it distilled like the example 1 except having not supplied molecular oxygen to a bottom. Consequently, after working for 17 days, the draw of liquid became impossible from the bottom. It stops, and when checked, about 1kg polymerization object adhered to the bottom section, and it was blocking draw piping of the bottom section. Although days of operation are twice [ more than ] the example of a comparison, it turns out that it is desirable to supply molecular oxygen.

[0027] In the [example 3] example 1, it distilled like the example 1 except having made temperature of the liquid of a spray into 55 degrees C, and having sprinkled it. Consequently, since the polymerization object was checked by the extract liquid after operation on the 25th, when it stopped and checked, about 0.5kg polymerization object had adhered to the bottom section.

[0028] Esterification reaction distillation of 2-ethylhexyl alcohol and an acrylic acid was performed using the stirred-tank-type reactor with a [example 4] bore [ of 3500mm ], and a body height of 3500mm made from stainless steel (SUS316), and the packed column with a bore [ of 1100mm ] installed in the upper part, and a restoration height (packing: cascade mini Ring 2 P) of 5000mm made from stainless steel (SUS316). the column top temperature under reaction distillation -- 43 degrees C and a pressure -- the reaction temperature of 8kPa(s) (absolute pressure) and a reactor -- 90 degrees C -- carrying out -- as a catalyst -- ion-exchange resin -- using -- a column -- phenothiazin 100ppm from the upper part -- from the contained 2-ethylhexyl alcohol and the reactor upper part, the acrylic-acid content liquid containing 200 ppm of METOKINON was supplied. Furthermore, continuous running of the air was supplied and carried out from the reactor lower part under the conditions of 0.15vol(s).% to the amount of overhead vapor (reference condition conversion).

[0029] a part of reaction mixture extracted from the reactor at that time -- using -- two baffles (path 200mmphi) -- respectively -- 500l. / hr (getting wet -- volume --) When it sprinkled in 1.6m3/m2hr and

an up manhole (path 500mmphi) with die length of 500mm which gets wet by the spray of 500l. / hr (it gets wet and is 1.6m<sup>3</sup>/m<sup>2</sup>hr at volume and die length of 500mm which gets wet), it was able to operate favorably for about one month.

[0030] Reaction distillation was performed like the example 3 except having not performed the [example 2 of comparison] spray. Consequently, since the polymerization object was seen by reaction draw liquid after operation on the 20th, when it stopped and checked, about 2kg polymerization object had adhered to the baffle, the agitator, and the manhole.

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[Translation done.]

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** It is the approximate account Fig. showing the example of representation of the distillation approach.

**[Drawing 2]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 3]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 4]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 5]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 6]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 7]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Drawing 8]** It is the approximate account Fig. showing the polymerization prevention approach concerning this invention.

**[Description of Notations]**

1 Distillation Apparatus

2 Condenser

3 Reboiler

4 Manhole

5 Atomization Injection Means

6 Pump

7 End Plate

8 Vapor Line

9 Atomization Injection Means

10 Tray

10a Downcomer

11 Vapour Chimney

12 Atomization Injection Means

13 Pump

14 Restoration Type Distillation Apparatus

15 Packed Bed

16 Supporter Material

17 Atomization Injection Means

18 Reactor

19 Distilling Column

20 Baffle  
21 Agitator  
22 Pump  
23 Oily Water Separation Tub  
24 Condenser  
25 Atomization Injection Means  
26 Manhole

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[Translation done.]

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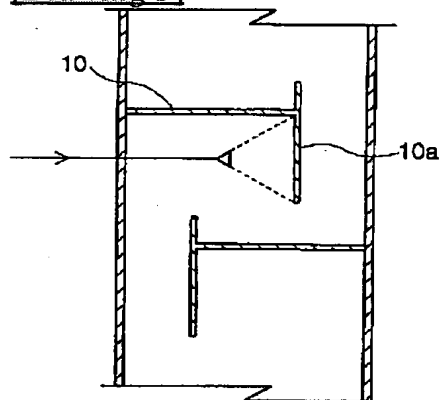
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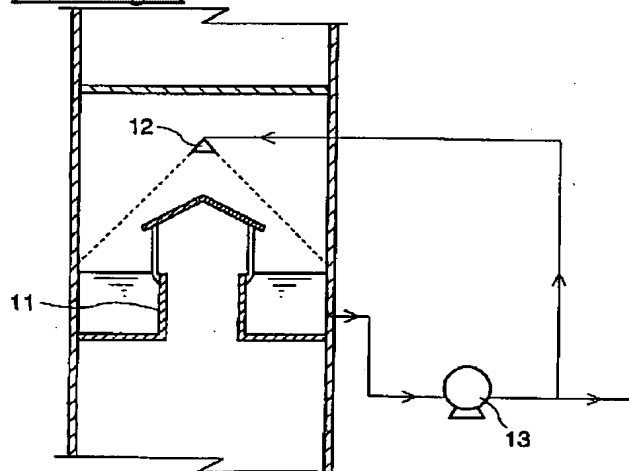
DRAWINGS

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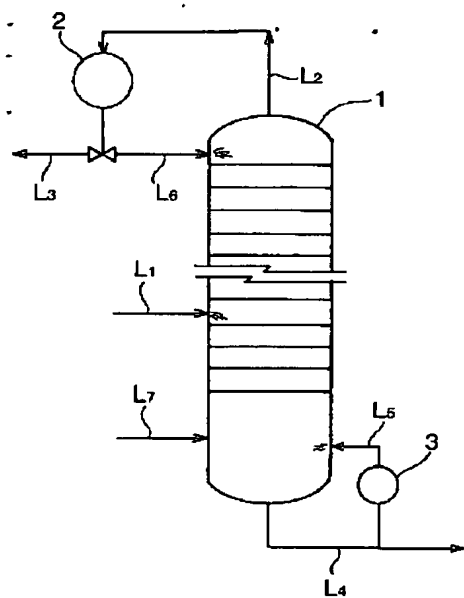
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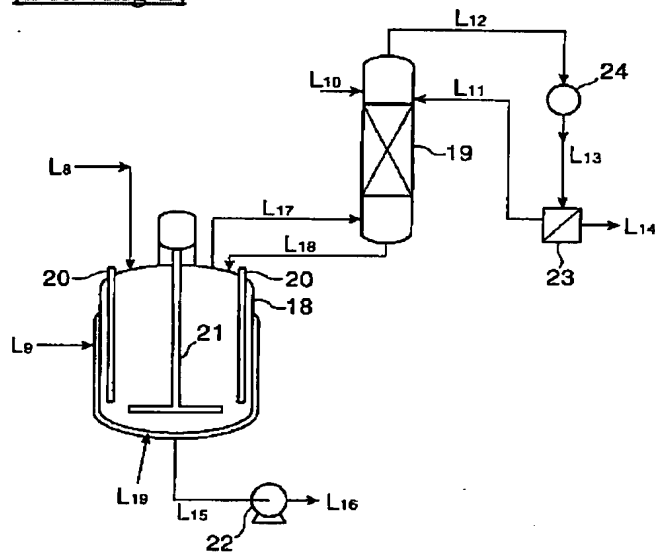
[Drawing 6]



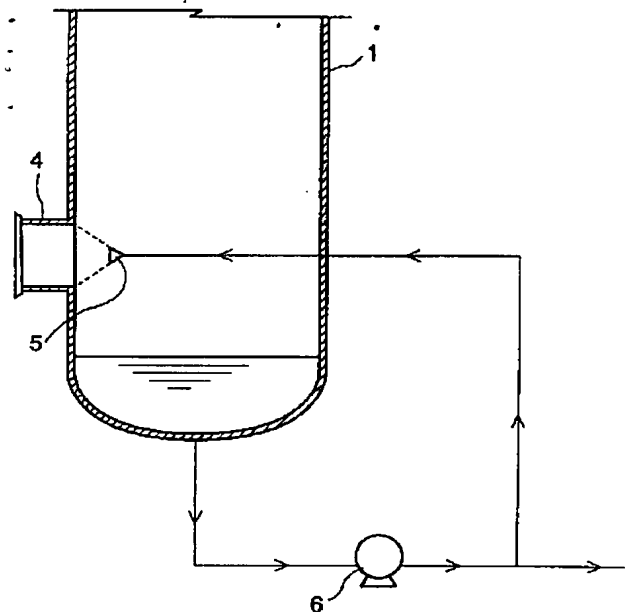
[Drawing 1]



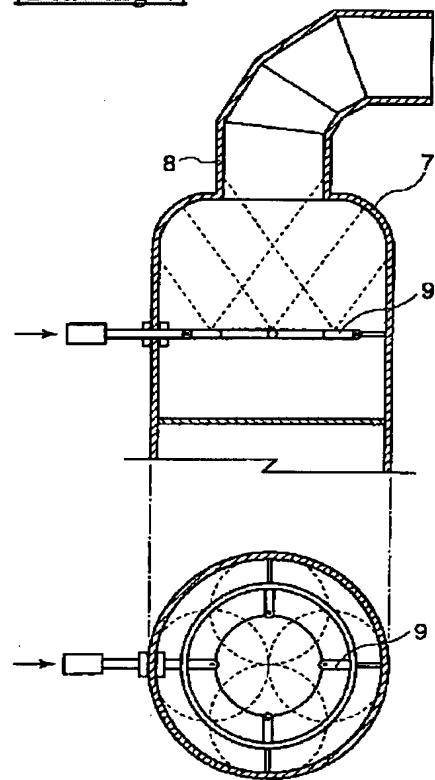
[Drawing 2]



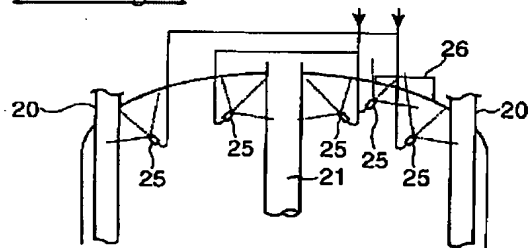
[Drawing 3]



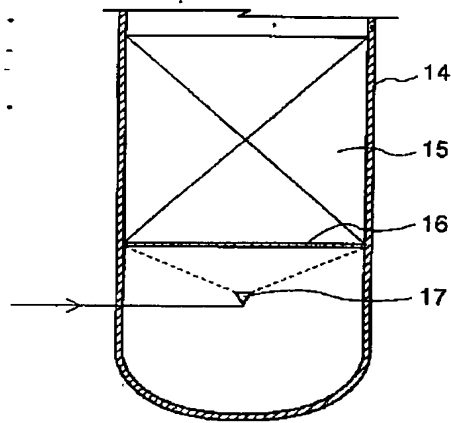
[Drawing 4]



[Drawing 8]



[Drawing 7]



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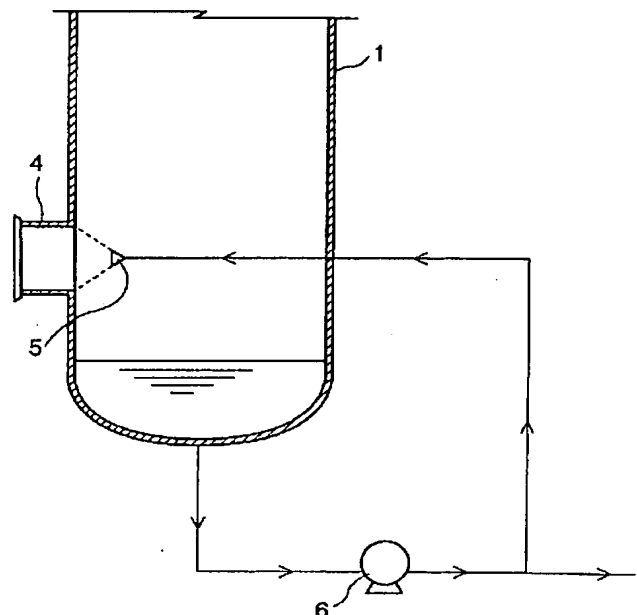
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(54) 【発明の名称】 易重合性化合物の重合防止方法

(57) 【要約】

【課題】 (メタ) アクリル酸や (メタ) アクリル酸エステル等の易重合性化合物を蒸留するにあたり、蒸留装置内部で発生しやすい重合を防止できる方法を提供する。

【解決手段】 蒸留装置を用い易重合性化合物を蒸留する方法において、蒸留装置内部に配設された構成部材に対して、該構成部材の周囲に存在する液と実質的に同一組成の液を、噴霧化投入手段で供給する。尚、前記噴霧化投入手段で供給する液は、上記構成部材の周囲の液温以下の温度に設定することが好ましい。



## 【特許請求の範囲】

【請求項 1】 蒸留装置を用いて易重合性化合物を蒸留する方法であって、蒸留装置内部に配設された構成部材に対して、該構成部材の周囲に存在する液と実質的に同一組成の液を、噴霧化投入手段で供給することを特徴とする易重合性化合物の重合防止方法。

【請求項 2】 前記噴霧化投入手段で供給する液の温度が、前記構成部材の周囲の液温以下である請求項 1 に記載の重合防止方法。

【請求項 3】 前記噴霧化投入手段で供給する液の濡れ液量を、前記構成部材の表面積に対して  $0.5 \text{ m}^3/\text{m}^2$  Hr 以上とする請求項 1 または 2 に記載の重合防止方法。

【請求項 4】 前記噴霧化投入手段で供給する液が重合禁止剤を含んでいる請求項 1 ～ 3 のいずれかに記載の重合防止方法。

【請求項 5】 前記蒸留装置に分子状酸素含有ガスを供給する請求項 1 ～ 4 のいずれかに記載の重合防止方法。

【請求項 6】 前記構成部材が、トレイ支持部材、充填物支持部材、フランジ、ノズル、鏡板、塔壁、チムニー、ダウンカマー、バッフル、攪拌軸である請求項 1 ～ 5 のいずれかに記載の重合防止方法。

【請求項 7】 前記易重合性化合物が、(メタ) アクリル酸及び/又は (メタ) アクリル酸エステルである請求項 1 ～ 6 のいずれかに記載の重合防止方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は (メタ) アクリル酸や (メタ) アクリル酸エステルなどの易重合性化合物を蒸留する際の重合を防止する方法に関するものである。

## 【0002】

【従来の技術】 蒸留は沸点の異なる 2 種以上の液体混合物からなる原料液を加熱気化し、低沸点成分を主体とする蒸気を凝縮して液体混合物の成分分離を行う操作であり、成分間の相対揮発度の違いが大きい場合には、成分の分離が容易である。但し、通常では、液の一部を気化・凝縮させるだけでは期待する濃度で成分の分離はできないので、凝縮液の一部を塔頂から棚段や充填物の表面に還流し、蒸留装置を上昇する蒸気と塔頂から流下する液を適切に接触させることにより、低沸点成分を塔頂から留出し、高沸成分を塔底から取り出すことが一般的である。尚、蒸留装置としては、蒸留塔や、薄膜蒸発器及び蒸留塔を備えた反応器などがあり、必要に応じてコンデンサー、リボイラー、外部加熱手段などが設置されている。また、薄膜蒸発器の場合には、更に上部に塔を設置することもある。

【0003】 図 1 は、(メタ) アクリル酸や (メタ) アクリル酸エステル [以下、(メタ) アクリル酸等ということがある] の蒸留に汎用されている棚段式蒸留装置 1 の断面説明図の 1 例であり、上記 (メタ) アクリル酸等

を主体とし、酢酸を不純物として含有する原料液を用いる場合を例に挙げて説明する。上記原料液は、塔壁より蒸留装置内へ供給される ( $L_1$ )。低沸点成分である酢酸は、塔内における加熱により気化して塔内を上昇し、塔頂から凝縮器 2 へ送られ ( $L_2$ ) 凝縮された後、系外に取り出される ( $L_3$ )。一方、(メタ) アクリル酸等の高沸点成分は塔底より次工程に送液され ( $L_4$ )、一部の精製液はリボイラー 3 を介して蒸留装置へ戻される ( $L_5$ )。尚、凝縮液には、不純物である酢酸だけでなく上記 (メタ) アクリル酸等も含んでいることから、(メタ) アクリル酸等の収率を向上させることを目的としてその一部は還流液として塔内へ戻され ( $L_6$ )、蒸留装置内で再度気液接触させることにより上記 (メタ) アクリル酸等は塔底に流下させるものである。

【0004】 また図 2 は、(メタ) アクリル酸エステルの反応に汎用されている説明図の一例である。触媒としてイオン交換樹脂を有する反応器 18 には (メタ) アクリル酸と、アルコールを含有する液が供給され ( $L_9$ )、攪拌機 21 で攪拌し、反応器ジャケットにスチーム投入することにより ( $L_9$ )、反応させながら蒸留により生成水をベーパーとして追い出す ( $L_{17}$ )。エステル化された (メタ) アクリル酸エステル含有液は ( $L_{15}$ ) から抜き出し、精製工程へ送液する ( $L_{16}$ )。反応器 18 からのベーパーは上部に設置した蒸留塔に供給し ( $L_{17}$ )、塔上部からの液供給 ( $L_{10}$ ,  $L_{11}$ ) で気液接触させ、エステル、(メタ) アクリル酸、アルコールなどの液は反応器に流下する ( $L_{18}$ )。塔上部からのベーパーは、凝縮器 24 に送られ ( $L_{12}$ ) 凝縮された後、油水分離槽 23 へ送られる ( $L_{13}$ )。油水分離後の水相は排出され ( $L_{14}$ )、油相は蒸留塔 17 に還流される ( $L_{11}$ )。また、必要に応じて、塔上部からアルコールが供給される様に構成されている ( $L_{10}$ )。

【0005】 ところで、上記 (メタ) アクリル酸等は、非常に重合しやすい化合物であることから、上記原料液や還流液には、ハイドロキノンやフェノチアジン等の重合禁止剤を含有させることが一般的であり、更には蒸留装置の下部 ( $L_7$ ) から分子状酸素含有ガスを供給して重合を抑制する方法も採用されている。

【0006】 また、これらの方法以外としては、特公昭 63-11921 号公報に、蒸留装置の蒸発面上下に外部加熱手段 (例えば、加熱ジャケット) を設置することにより、気相部器壁などにおいて蒸気が凝縮して重合防止剤のない状態で凝縮液が重合することを防止する方法が開示されている。

【0007】 しかしながら、重合は必ずしも防止されおらず、重合の発生により、しだいに精製効率が低下してしまうことから、蒸留装置の運転を停止し重合物の除去作業を行うことが比較的頻繁に行われていた。

## 【0008】

【発明が解決しようとする課題】 本発明は上記事情に着

目してなされたものであり、(メタ)アクリル酸や(メタ)アクリル酸エステル等の易重合性化合物を蒸留するにあたり、蒸留装置内部で発生しやすい重合を防止する方法を提供しようとするものである。

#### 【0009】

【課題を解決するための手段】上記課題を解決した本発明の重合防止方法とは、蒸留装置を用いて易重合性化合物を蒸留する方法であって、蒸留装置内部に配設された構成部材に対して、該構成部材の周囲に存在する液と実質的に同一組成の液を、噴霧化投入手段で供給することを要旨とするものである。尚、前記噴霧化投入手段で供給する液は、上記構成部材の周囲の液温以下に(周囲に存在する液の温度と同じか、或いは低く)することが望ましい。また濡れ液量(噴霧化して供給した液分の内、構成部材上に付着して構成部材を濡らした液量)を、前記構成部材の表面積に対して $0.5 \text{ m}^3/\text{m}^2 \text{ Hr}$ 以上とすることが望ましく、また上記噴霧化投入手段で供給する液は重合禁止剤を含有させることが推奨され、更に上記蒸留装置には分子状酸素含有ガスを供給することが望ましい。尚、分子状酸素含有ガスとしては、酸素ガスの他、空気を用いることができる。分子状酸素含有ガスの供給量(該ガスが酸素ガス以外の成分を含有する場合には酸素ガスとしての供給量)は、気相中に存在する易重合性化合物の蒸発蒸気量(標準状態換算)の $0.01 \sim 5$ 容量%であることが好ましく、 $0.02 \sim 3$ 容量%であればより好ましい。

【0010】前記構成部材としては、トレイ支持部材、充填物支持部材、フランジ、ノズル、鏡板(平形、皿形、半楕円形、半球形、円錐体形等)、塔壁、チムニー、ダウンカマー、パッフル、攪拌軸等が挙げられ、前記易重合性化合物としては、(メタ)アクリル酸や(メタ)アクリル酸エステル等が例示できる。

#### 【0011】

【発明の実施の形態】蒸留装置を用いて易重合性化合物を蒸留する際には、易重合性化合物が蒸留装置内部の構成部材表面で停滞することにより(即ち、同一の液が同一の場所に停滞することにより)重合するものである。特に、気相が凝縮した液が構成部材上で停滞した場合には、重合禁止剤がほとんど含まれていない液体として停滞するので、重合物の量が多くなりやすく、しばしば運転をストップさせる原因となっていた。

【0012】本発明者らは、アクリル酸等の易重合性化合物を蒸留する際に、蒸留装置内部の構成部材表面で液体の滞留がないようにして蒸留を行うと蒸留装置内での重合を効果的に防止でき、そのためには構成部材表面の全面に亘って構成部材の周囲に存在している液と実質的に同一組成の液を用いて散布すればよいことを見出し、本発明に想到した。さらに散布液の液温を構成部材の周囲に存在している液の温度と同一にするか、或いは低くすることが好ましく、更には重合禁止剤を含有させれば

望ましく、蒸留装置内に分子状酸素が存在すると一層効果が顕著である。

【0013】蒸留装置内の構成部材に散布する液体は、構成部材の周囲に存在している液と実質的に同一組成の液である。具体的には、フィード液(原料液)、塔内からの拔出し液、還流液、ボトム循環液(精製液)等を用いればよく、これらの液体の一部または全部を散布すればよい。また、これらの液は構成部材の周囲に存在している液よりも易重合性化合物が低濃度または低粘度であることが好ましく、蒸留の運転操作に問題のない程度に、この液を水、アルコール、共沸溶剤、抽出溶剤等が希釈して、より低い濃度または粘度にして散布することが推奨される。

【0014】更に、構成部材に供給する液の温度が、構成部材の周囲の温度より高い場合には、供給液の一部が蒸発して液の散布が不安定となるので、蒸留装置内の構成部材の周囲温度以下の液を供給することが好ましい。尚、供給液の温度が低すぎると、構成部材周囲のガスが凝縮し過ぎて重合防止効果が減少するので、供給液温度は蒸留装置内の構成部材の周囲温度よりも $0 \sim 40^\circ\text{C}$ 低くすることが好ましく、 $1 \sim 30^\circ\text{C}$ 以下であればより望ましい。

【0015】重合禁止剤としては、ハイドロキノン、フェノチアジン、メトキノン、酢酸マンガ、ニトロソフェノール、クペロン、N-オキシル化合物、ジブチルチオカルバミン酸銅などが知られており、上記重合禁止剤を易重合性化合物や溶剤などに溶解させ、フィード液や還流液、ボトム循環液の供給ラインに投入するか、直接蒸留装置内に供給すればよい。尚、ボトム循環液には、通常、蒸留装置に投入された重合禁止剤が比較的多量に含有されているので、新たに重合禁止剤を加えなくても、蒸留装置内に戻し構成部材に散布すればよい。

【0016】重合を防止する上で、分子状酸素含有ガスを供給することが推奨され、上記分子状酸素含有ガスは、酸素濃度が低いと重合防止に必要な分子状酸素ガス量が多くなり、真空装置での容量が大きくなると共に、蒸留装置、真空装置での重合物の量が多くなることから、空気の酸素濃度( $20 \sim 21 \text{ vol}\%$ )以上であることが望ましく、 $40 \sim 100 \text{ vol}\%$ であればより望ましく、 $80 \sim 100 \text{ vol}\%$ であればより一層望ましい。

【0017】本発明方法では、蒸留装置内の構成部材に対して、その全面を均一に濡らす様に、噴霧化投入手段(スプレー)で液を散布するものであるが、スプレーのタイプやノズル数、流量等の噴霧化の条件は、構成部材の配設位置や、蒸留装置内の雰囲気に応じて適宜設定すればよいが、いずれにしても構成部材の全面をできるだけ均一に濡らすように設定することが望ましい。

【0018】また噴霧液量が、構成部材表面積に対して、濡れ液量が $0.5 \text{ m}^3/\text{m}^2 \text{ Hr}$ 以上であれば好まし

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く、 $1\text{ m}^3/\text{m}^2\text{ Hr}$  以上であればより望ましく、 $2\text{ m}^3/\text{m}^2\text{ Hr}$  以上であればより一層望ましい。尚、上記構成部材表面積とは、フランジやノズルについては、 $(\pi/4) D^2$  (但し、 $D$  は直径) で表わされる面積であり、その他の部材については、液噴霧ノズルの広がり角度と構成部材表面との距離で算出できる濡れ面積を言う。

【0019】蒸留装置内に配設されている構成部材としては、トレイ支持部材、充填物支持部材、フランジ、ノズル、鏡板、塔壁、チムニー、ダウンカマー、バフ、10 攪拌軸等がある。尚、本発明でノズルとは、蒸留装置に設置されているものすべてを含むものであり、ガスや液の入口または出口ノズルをはじめ、マンホール、計装機器座 (圧力計座、液面計座、温度計座等) などが挙げられる。このような構成部材であって、気相の凝縮により生成した液が停滞して重合が発生し易い箇所に液をスプレーし液の停滞を防止することにより重合発生を防止することができる。また、液相部についても、噴霧液により停滞している液を移動させることにより、重合を防止することができる。

【0020】本発明に係る易重合性化合物の好適な例としては、(メタ) アクリル酸と (メタ) アクリル酸エステルが挙げられ、後者の例としては、メチルエステル、エチルエステル、イソプロピルエステル、 $n$ -プロピルエステル、イソブチルエステル、 $n$ -ブチルエステル、2-エチルヘキシルエステル、2-ヒドロキシエチルエステル、ヒドロキシプロピルエステル、ジアルキルアミノエチルエステル等が挙げられるが、中でも最も容易に重合しやすい (メタ) アクリル酸に対して本発明方法は非常に効果的である。

【0021】図3~8は、いずれも本発明例を示す概略説明図であり、図3は蒸留装置1の下部に設けられているマンホール4に対して、塔底から導出された精製液を蒸留装置1に戻し、噴霧化投入手段5によりスプレーする方法を示している。図4は、塔頂に配設された鏡板7及び/又は塔頂から次工程の凝縮器へのペーパーライン8に対して、噴出口を4か所に有する噴霧化投入手段9により還流液をスプレーする方法を示している。図5は、棚段式蒸留装置のトレイ10下部のダウンカマー10aに対して、原料液を投入する方法を示している。図6は、蒸留装置内の途中から液を抜き出す目的で配設されたチムニー11に対して、抜き出し液の一部を戻し、噴霧化投入手段12によりスプレーする方法を示している。図7は、充填式蒸留装置14において、充填層15の支持部材16に対して液を噴霧化投入手段17によりスプレーする方法を示している。図8は、反応蒸留する反応器において、攪拌機21、バフ20、マンホール26に対して、噴霧化投入手段25によりスプレーする方法を示している。また図3~8は、気相部の気相が凝縮した液の重合ばかりでなく、噴霧液の液相部への落

下により、液の移動を起こさせ、滞留時間を少なくし、重合を防止する例を示すものでもある。

【0022】以下、本発明を実施例によって更に詳細に説明するが、下記実施例は本発明を限定する性質のものではなく、前・後記の主旨に基づいて設計変更することはいずれも本発明の技術的範囲に含まれるものである。

【0023】

【実施例】 [実施例1] 内径1300mm、段数50段のステンレス鋼製 (SUS316) のシーブトレイを内装したステンレス鋼製 (SUS316) の蒸留装置を用い、アクリル酸の精製を行った。蒸留中の塔頂の温度は63℃、圧力は4.7kPa (35mmHg) とし、塔底の温度は100℃、還流比は1.8に設定した。原料液には、重合防止剤としてフェノチアジンを50ppm含有させ、還流液には、メトキノンと100ppm含有させた。更に塔底から塔頂ペーパー量 (標準状態換算) に対して分子状酸素を0.3vol.%の条件下で供給して連続運転した。

【0024】その際、ボトム循環液を使って、塔底のマンホール (径500mmφ) に500リットル/hの流量 (濡れ液量  $2.5\text{ m}^3/\text{m}^2\text{ Hr}$ ) のスプレーで90℃の液を全面に散布したところ、約1ヶ月間順調に運転することができた。

【0025】 [比較例1] 塔底のマンホールにスプレーを行わなかったこと以外は、実施例と同様にして、蒸留を行った。その結果、8日間稼動した後、塔底より液抜き出しが不可能になった。停止して点検したところ、塔底部に約2kgの重合物が付着しており、それが塔底部の抜き出し配管を詰まらせていた。

【0026】 [実施例2] 実施例1において、塔底に分子状酸素を供給しなかったこと以外は、実施例1と同様にして蒸留を行った。その結果、17日間稼動した後、塔底より液の抜き出しが不可能になった。停止して点検してみたところ、塔底部に約1kgの重合物が付着し、それが塔底部の抜き出し配管を詰まらせていた。稼働日数は比較例の2倍以上であるものの、分子状酸素を供給することが望ましいことが分かる。

【0027】 [実施例3] 実施例1において、スプレーの液の温度を55℃にして散布したこと以外は、実施例1と同様にして蒸留を行った。その結果、25日稼働後の抜き出し液に重合物が確認されたので、停止して点検したところ、塔底部に約0.5kgの重合物が付着していた。

【0028】 [実施例4] 内径3500mm、直胴高さ3500mmのステンレス鋼製 (SUS316) の攪拌槽型反応器と、上部に設置した内径1100mm、充填高さ (充填物: カスケードミニリング2P) 5000mmのステンレス鋼製 (SUS316) の充填塔を用い、2-エチルヘキシルアルコールとアクリル酸のエステル化反応蒸留を行った。反応蒸留中の塔頂温度は43℃、圧力は8kPa (絶対圧力)、反応器の反応温度は90

℃とし、触媒としてイオン交換樹脂を用い、塔上部からフェノチアジン100ppm含有した2-エチルヘキシルアルコール、反応器上部からは、メトキノンに200ppm含有したアクリル酸含有液を供給した。更に、反応器下部から塔頂ペーパー量（標準状態換算）に対して空気を0.15vol.%の条件下で供給して連続運転した。

【0029】その際、反応器から抜き出した反応液の一部を使って、バッフル（径200mmφ）2本に夫々500リットル/hr（濡れ液量、濡れる長さ500mmで $1.6\text{ m}^3/\text{m}^2\text{ hr}$ ）、上部マンホール（径500mmφ）に500リットル/hr（濡れ液量、濡れる長さ500mmで $1.6\text{ m}^3/\text{m}^2\text{ hr}$ ）のスプレーで散布したところ、約1ヶ月順調に運転することができた。

【0030】【比較例2】スプレーを行わなかったこと以外は、実施例3と同様にして反応蒸留を行った。その結果、20日稼働後、反応抜き出し液に重合物がみられたため、停止して点検したところ、バッフル、攪拌機、マンホールに約2kgの重合物が付着していた。

【0031】

【発明の効果】本発明は以上の様に構成されているので、（メタ）アクリル酸や（メタ）アクリル酸エステル等の易重合性化合物を蒸留するにあたり、重合を防止する方法が提供できることとなった。

【図面の簡単な説明】

【図1】蒸留方法の代表例を示す概略説明図である。

【図2】本発明に係る重合防止方法を示す概略説明図である。

【図3】本発明に係る重合防止方法を示す概略説明図である。

【図4】本発明に係る重合防止方法を示す概略説明図である。

【図5】本発明に係る重合防止方法を示す概略説明図である。

\* 【図6】本発明に係る重合防止方法を示す概略説明図である。

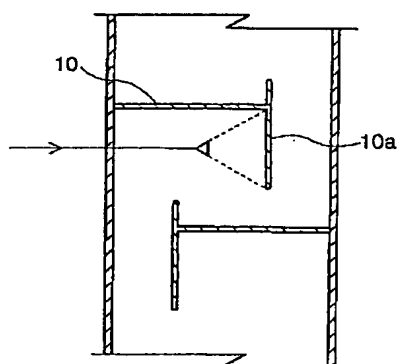
【図7】本発明に係る重合防止方法を示す概略説明図である。

【図8】本発明に係る重合防止方法を示す概略説明図である。

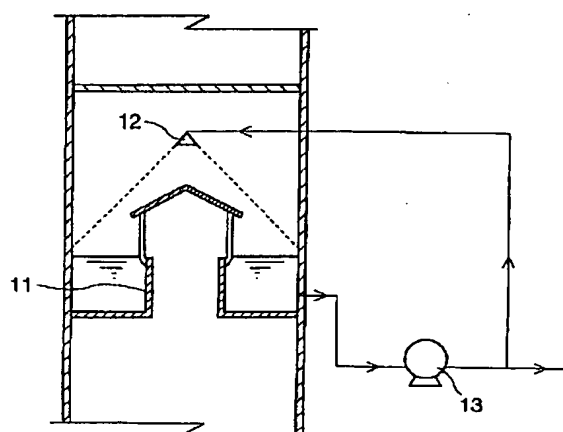
【符号の説明】

- |     |            |
|-----|------------|
| 1   | 蒸留装置       |
| 2   | 凝縮器        |
| 3   | リボイラー      |
| 4   | マンホール      |
| 5   | 噴霧化投入手段    |
| 6   | ポンプ        |
| 7   | 鏡板         |
| 8   | ペーパーライン    |
| 9   | 噴霧化投入手段    |
| 10  | トレイ        |
| 10a | ダウンカマー     |
| 11  | チムニー       |
| 20  | 12 噴霧化投入手段 |
| 13  | ポンプ        |
| 14  | 充填式蒸留装置    |
| 15  | 充填層        |
| 16  | 支持部材       |
| 17  | 噴霧化投入手段    |
| 18  | 反応器        |
| 19  | 蒸留塔        |
| 20  | バッフル       |
| 21  | 攪拌機        |
| 30  | 22 ポンプ     |
| 23  | 油水分離槽      |
| 24  | 凝縮器        |
| 25  | 噴霧化投入手段    |
| *   | 26 マンホール   |

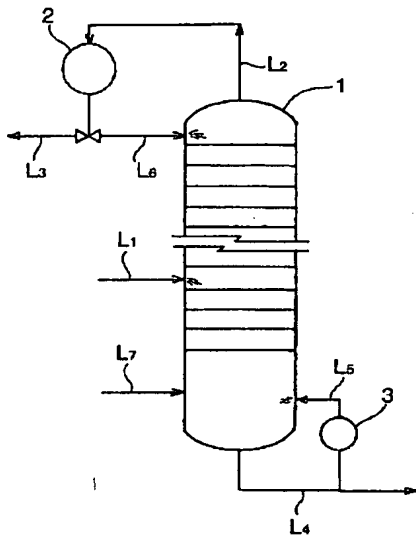
【図5】



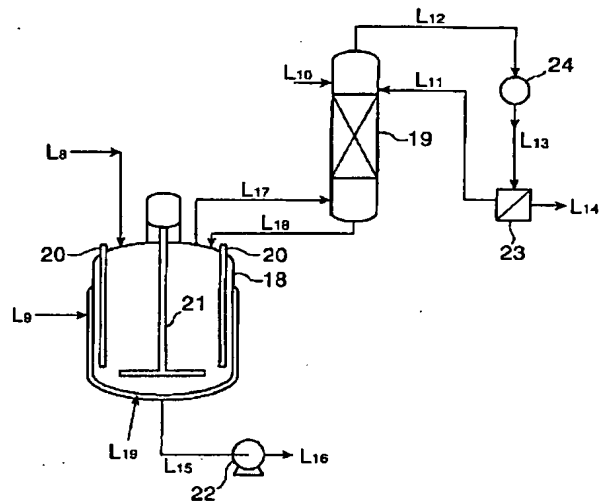
【図6】



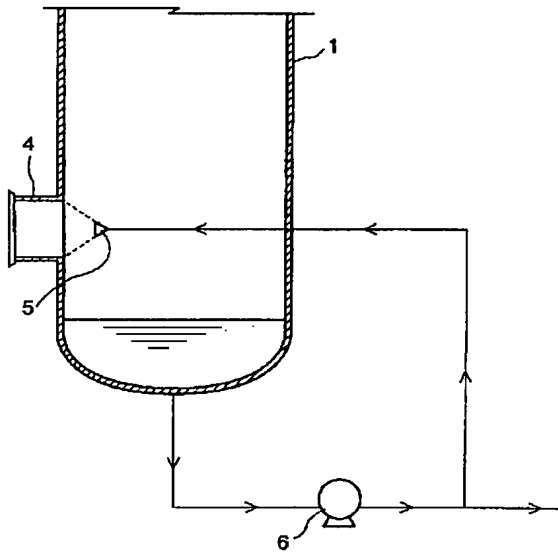
【図 1】



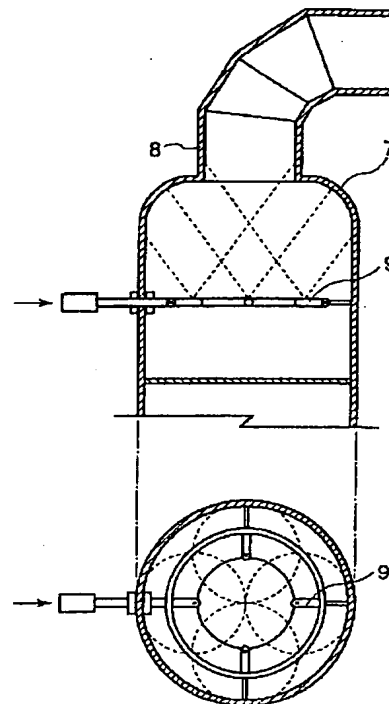
【図 2】



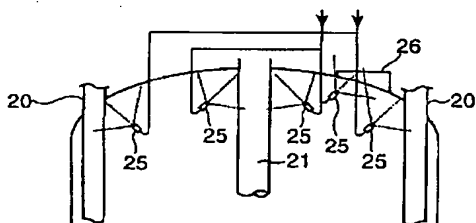
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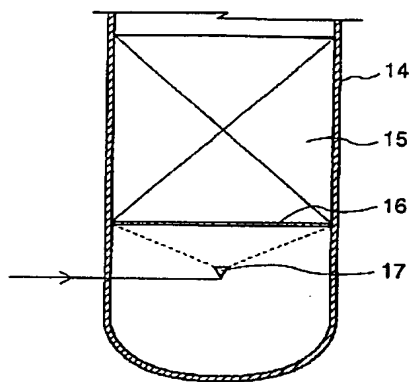
【図 4】



【図 8】



【図 7】



フロントページの続き

(51) Int. Cl.<sup>7</sup>

C 0 7 C 57/04  
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67/62  
69/653

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69/653

テーマコード (参考)

English translation of Japanese Patent Application Laid-Open  
(KOKAI) No. 47-10614 (Laid Open Date: May 27, 1972)

1. TITLE OF THE INVENTION

PROCESS FOR PRODUCING ACRYLIC ACID

2. SCOPE OF THE INVENTION:

1. A process for producing acrylic acid comprising a first reaction stage of oxidizing propylene into substantially acrolein in a reaction tube filled with a catalyst by using a mixed gas containing an inert diluting gas containing elementary oxygen and water vapor; and a second reaction stage of further oxidizing the acrolein into acrylic acid, wherein the propylene is oxidized under such a condition that an initial concentration of the propylene is more than 2 mol% based on a starting mixed gas, and at both the reaction stages, a space load in each reaction stage is controlled to more than 60 L/hr propylene per 1 L of the catalyst,

characterized in that an activity of the catalyst is changed through the two stages so as to increase up to 100% either continuously or stepwise from an inlet of the reaction tube along the direction of the reaction tube, and a reaction waste gas from which a majority of a condensable gas obtained in an outlet of the second reaction stage is



removed, is re-fed to the first reaction stage in place of a part or a whole of the water vapor as the inert diluting gas.

### 3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for producing acrylic acid by subjecting propylene to a two-stage oxidation via an intermediate stage for obtaining acrolein therefrom, using an oxidation catalyst.

It is known that propylene is oxidized in a gas phase on a solid catalyst in the presence of an oxygen-containing gas and water vapor at an enhanced temperature to produce acrylic acid. In this case, the propylene is oxidized mainly into acrolein at a first stage, and then the resultant reaction mixed gas is oxidized in a second stage on a second catalyst without separating the acrolein therefrom to produce acrylic acid.

For the first stage, there have been proposed the catalyst systems containing elements belonging to Groups IVa to VIa, VIII and IVb to VIIb of the Periodic Table. Among these catalyst systems, tellurium-containing catalysts (those catalysts containing tellurium dioxide or telluric acid or catalysts of this type containing bismuth or antimony and optionally phosphorus) are more excellent, in particular, because of a high selectivity to production of acrolein at a relatively low both temperature of a nitre

bath reactor normally used for the reaction. In this case, there may also be used catalysts containing molybdenum, tungsten and tellurium oxide, or cobalt, molybdenum and tellurium oxide. The other proposed catalysts contain, for example, iron, tin, antimony and vanadium, or nickel, cobalt, iron, bismuth, phosphorus and molybdenum, in addition to oxygen, and samarium oxide and tantalum oxide are optionally added thereto in some cases. The production and use of the above catalyst systems for oxidizing propylene into acrolein are described, for example, in the specifications of German Patent Applications Nos. P 15 42 030.1 and P 16 43 737.9.

Although the oxidation catalysts containing the elements selected from the above groups are also preferably used for the second stage, there is generally such a limitation that the elements belonging to the Groups Va and VIa of the Periodic Table should not be used, in particular, none or only a slight amount of selenium or tellurium should be used, in order to further oxidize and convert acrolein into acrylic acid as completely as possible. The conventionally known catalysts contain, for example, cobalt and molybdenum, or molybdenum, tungsten and vanadium, or tin, antimony and molybdenum, in addition to oxygen.

The catalyst used advantageously contains, in addition to oxygen, molybdenum, tungsten, as well as iron and(/or) nickel and(/or) manganese and(/or) copper and optionally

vanadium. The production of the catalyst and the use thereof for oxidizing acrolein into acrylic acid are described in the specifications of German Patent Application Nos. P 16 18 133.2 and P 19 08 965.7.

The teachings of the above literatures aim at finally achieving production of acrylic acid with as high an absolute yield as possible relative to propylene. However, other problems which are also important for conducting the above process are not taken into consideration to a sufficient extent.

The most important problems are a space time yield and a concentration of acrylic acid in the resultant condensate. In the experiments using industrial apparatuses, it has been considerably difficult to produce the acrylic acid with a high space time yield and a high concentration. In the industrial single-stage or multi-stage method for synthesis of acrylic acid by a gas phase oxidation, rapid removal of reaction heat locally generated which is required to attain a high conversion rate of propylene in one passage becomes possible only by taking a too uneconomical measure for solving the problem. For example, by selecting a reaction tube having a narrow section or operating at a low temperature, therefore, under a low catalyst load and a low tube load (linear gas velocity), and further diluting the gas to be oxidized with a large amount (up to 40% by volume)

of water vapor, the process must be protected against explosive combustion on the catalyst or at least excessive oxidation by which undesirable byproducts are produced. The acrylic acid may be obtained with a relatively high absolute yield which reaches not less than 50% of a theoretical value thereof relative to propylene used. However, in order to achieve such a high yield, it is required to conduct the process under a low space load (long residence time), and further since the acrylic acid is produced only in the form of an extremely dilute aqueous solution, uneconomically high energy costs and investments are required.

The technical tendency has been directed to enhancement of space time yield so as to achieve an economical process as a whole according to such a guideline that enables high absolute yield only by one passage as attained by conventional endeavors. An object of the present invention is to develop a safe oxidation method capable of minimizing the above excessive oxidation and surely preventing the explosive combustion process.

The present inventors have found that the above object can be achieved by a process for producing acrylic acid comprising a first reaction stage of oxidizing propylene into substantially acrolein in a reaction tube filled with a catalyst by using a mixed gas containing an inert diluting gas containing elementary oxygen and water vapor; and a

second reaction stage of further oxidizing the acrolein into acrylic acid, wherein the propylene is oxidized under such a condition that an initial concentration of the propylene is more than 2 mol% based on a starting mixed gas, and at both the reaction stages, a space load in each reaction stage is controlled to more than 60 L/hr propylene per 1 L of the catalyst,

characterized in that an activity of the catalyst is changed through the two stages so as to increase up to 100% either continuously or stepwise from an inlet to an outlet of the reaction tube, and a reaction waste gas from which a majority of a condensable gas obtained in an outlet of the second reaction stage is removed, is re-fed to the first reaction stage in place of a part or a whole of the water vapor as the inert diluting gas.

According to the above process, it is possible to prevent the resultant acrylic acid to be produced in the form of a dilute solution in which the acrylic acid is diluted with a too large amount of water. Therefore, the finish treatment for obtaining pure acrylic acid requires only an extremely short time and an extremely slight energy consumption. As a matter of course, as far as technical preconception of the processes of the above type is concerned, it has been considered that the absolute yield is remarkably deteriorated due to the dilution of an active

catalyst substance. However, unexpectedly, the results are different from the above preconception. According to the process of the present invention, in the reaction system of the above type, a substantially high space load can be attained, i.e., the amount of materials passed therethrough can be remarkably enhanced without any risks. In the process of the present invention, it is possible to obtain an absolute yield of about 50% relative to propylene used, similarly to the conventional processes.

The still other advantage of diluting the catalyst resides in that water vapor used for the synthesis is replaced with the fed-back reaction gas having a remarkably small heat capacity as compared to water vapor as known in the art, thereby preventing occurrence of risks of excessive oxidation and local overheating. With this advantage, the process of the present invention can be considerably improved in economy as compared to the conventional processes. This is because acrylic acid can be produced at a concentration of 50% by weight in the obtained condensate by the second means.

The process of the present invention is more specifically performed as follows. First, the concentration of propylene is controlled to more than 2 mol% based on a starting mixture, and the bath temperature as required is selected such that the rate of conversion of propylene or

acrolein exceeds 80 to 85 mol% irrespective of the specific catalyst system under a space load of more than 60 L/hr propylene.

In order to react the mixed gas, the active catalyst substance is diluted with an inert material to reduce a catalytic activity thereof. In this case, the diluting procedure is performed such that the activity of the catalyst is increased up to 100% either continuously or stepwise from an inlet to an outlet of the reaction tube. However, the activity of the catalyst preferably already reaches 100% prior to the end of the reaction tube. In this case, 5 to 50% by weight of the catalyst substance based on the whole catalyst substance is preferably diluted by the method of the present invention. In such a procedure, in particular, the dilution of 10 to 30% by weight of the catalyst substance is interested from the industrial viewpoints. In other words, the activity of the catalyst substance located subsequent to the position corresponding to a half length or shorter of the reaction tube preferably already reaches 100%. In the portion of the catalyst substance to be diluted, the degree of increase in dilution thereof depends upon a linear velocity of the gas. When the gas linear velocity becomes higher, in order to avoid occurrence of uncontrollable local temperature rise, the activity of the catalyst substance must be remarkably

reduced at an initial portion of the reaction tube. In accordance with the present invention, it is preferred that the activity or the content of an active substance in the layer to be diluted is increased from 0 to 100% as measured at a gas linear velocity of more than 60 cm/sec in an empty reaction tube. More preferably, after starting from the dilution of 25 to 75% of the active substance, the content of the active substance is increased to 100%. The diluent used for the above dilution is required to be selected from those substances inert to the reaction which have a heat stability withstanding a temperature of at least 600°C and preferably up to 700°C, are possibly made of a non-porous material and further free from formation of compounds with the catalyst component under the reaction conditions. Examples of the suitable diluent include oxide of aluminum, zirconium, titanium, magnesium or silicon which are treated at a high temperature, as well as silicates and aluminosilicates which are fused at a high temperature, electrode graphite, cement substances, and sintered materials fused at a high temperature. Among these substances, preferred are steatite,  $\alpha$ -alumina and silicon carbide.

The dilution is preferably conducted by mixing a catalyst molded product with a molded product made of an inert material having the same or substantially same size as



that of the catalyst molded product, or by first mixing the catalyst material and inert material both in the form of fine particles with each other and then molding the resultant mixture of these fine particles.

The reaction gas obtained after completion of the second reaction stage from which acrylic acid, water vapor and other condensable products are removed by cooling is added and mixed in the starting mixed gas fed to the first reaction stage which is almost composed of propylene, air and optionally water vapor. The mixing method and the amount of the reaction gas mixed may be determined in view of unreacted propylene and oxygen contained in the fed-back reaction waste gas such that the concentration of propylene prior to an inlet of the first catalyst layer is not less than 2 mol% and preferably 4 to 8 mol% based on the whole mixed gas, and the molar ratio between propylene, oxygen and water is 1: 1.5 to 4: 0 to 3 and preferably 1: 2 to 3: 0 to 2.

In the process of the present invention, it is advantageous that the catalyst used in the first reaction stage contains molybdenum, tungsten and tellurium in addition to oxygen, and has an atomic ratio of molybdenum to tungsten of 0.03 to 40: 1 and preferably 0.2 to 25: 1, a tellurium content of 0.2 to 2% by weight and preferably 0.5 to 1.8% by weight, whereas the catalyst used in the second

reaction stage contains molybdenum, tungsten, and iron and(/or) nickel and(/or) manganese and(/or) copper in addition to oxygen and further optionally contains vanadium, and has an atomic ratio between molybdenum, tungsten and iron [nickel, manganese and(/or) copper] of 1 to 20:0.01 to 10:1 and preferably 2 to 10: 0.1 to 2: 1, and an atomic ratio of molybdenum to vanadium of 6: 6 to 0.2 and preferably 6: 0.5 to 4. Further, other ordinary catalysts for oxidizing propylene into acrolein or oxidizing acrolein into acrylic acid may also be suitably used in the first and second reaction stages of the process of the present invention. Examples of the catalysts include those catalysts described in German Patent Nos. 1924496 and 200425, Belgian Patent Nos. 689720, 746202 and 738250, Netherlands Patent Application Laid-open No. 70.11603 and Japanese Patent Publication (KOKOKU) No. 45-22525(1970).

According to the process of the present invention, in the respective reaction stages, the bath temperature corresponding to a rate of conversion of not less than 80%, in particular, not less than 85%, and a yield of acrylic acid of 45 to 50 mol% can be realized under a tube load as high as not less than 60 L/hr propylene and preferably not less than 100 L/hr propylene per 1 L of the catalyst (L: each measured under normal condition) and at a gas linear velocity of not less than 60 cm/sec and preferably 100

cm/sec as measured in an empty reaction tube.

Examples 1 to 9:

In the following examples, it was indicated that when passing the reaction gas over the catalyst which was used initially under a considerably diluted condition and then at a continuously or stepwise increased concentration according to the process of the present invention, the space time yield was as high as about 2 to 3 times that obtained in the case of using a non-diluted catalyst. In this process, the space time yield was no longer enhanced by re-feed of a flue gas or a part thereof (Example 9) and substitution of water vapor associated therewith. On the contrary, the concentration of acrylic acid in the obtained aqueous solution was increased to 2 times.

The experiment was performed in detail as follows. A nitrogen mixture containing propylene (98%), air, water vapor and optionally 1.8% by volume of carbon monoxide was passed through a two-stage apparatus constituted from two tubes each having a length of 4 m and a diameter of 25 mm which were connected in series with each other. The respective tubes were placed in an electrically heatable salt bath capable of being agitated. Gases entering the tubes were respectively passed through a heat exchanger and preheated or pre-cooled to substantially a temperature of

the salt bath. A hot reaction gas having a temperature of 200 to 300°C which was discharged from the second reaction stage was cooled in a two stage quenching system by using the obtained condensate. The tube used in the first reaction stage was filled with a molybdenum/tungsten/tellurium catalyst, whereas the tube used in the second reaction stage was filled with a molybdenum/tungsten/vanadium/iron catalyst, and these catalysts were changed into the tubes of the respective reaction stages in the form of tablets each having a size of 3 x 3 mm. The charged materials were respectively diluted in the inlet layer by using steatite balls each having a diameter of 3 mm.

The conversion rates, acrylic acid yields, residual acrolein yields after the second reaction stage, space time yields and concentrations of acrylic acid in the obtained condensates with respect to catalyst amounts, dilution ratios, gas amounts and amounts of propylene (98%) entering the first reaction stage are shown in detail in Table 1.

Table 1

Examples	Amount of catalyst in each reaction tube (mL)	
	Tube 1	Tube 2
1	600 (active substance: 100% by volume)	300 (active substance: 100% by volume)
2	1000 (active substance: 100% by volume)	500 (active substance: 100% by volume)
3	400 (active substance: 25% by volume)	500 (active substance: 100% by volume)
	900 (active substance: 100% by volume)	
4	400 (active substance: 25% by volume)	400 (active substance: 25% by volume)
	900 (active substance: 100% by volume)	400 (active substance: 100% by volume)
5	400 (active substance: 25% by volume)	400 (active substance: 25% by volume)
	1100 (active substance: 100% by volume)	500 (active substance: 100% by volume)
6	200 (active substance: 25% by volume)	400 (active substance: 25% by volume)
	150 (active substance: 33% by volume)	700 (active substance: 100% by volume)
	100 (active substance: 50% by volume)	
	1050 (active substance: 100% by volume)	

Table 1 (continued)

Examples	Amount of catalyst in each reaction tube (mL)	
	Tube 1	Tube 2
7	200 (active substance: 25% by volume)	400 (active substance: 25% by volume)
	150 (active substance: 33% by volume)	700 (active substance: 100% by volume)
	100 (active substance: 50% by volume)	
	1050 (active substance: 100% by volume)	
8	120 (active substance: 25% by volume)	120 (active substance: 25% by volume)
	210 (active substance: 33% by volume)	210 (active substance: 33% by volume)
	140 (active substance: 50% by volume)	140 (active substance: 50% by volume)
	1030 (active substance: 100% by volume)	630 (active substance: 100% by volume)
9	120 (active substance: 25% by volume)	120 (active substance: 25% by volume)
	210 (active substance: 33% by volume)	210 (active substance: 33% by volume)
	140 (active substance: 50% by volume)	140 (active substance: 50% by volume)
	1030 (active substance: 100% by volume)	630 (active substance: 100% by volume)

Table 1 (continued)

Examples	Amount of gas (L/hr)			
	C <sub>3</sub> H <sub>6</sub>	Air	H <sub>2</sub> O	N <sub>2</sub> /Co
1	36	420	196	-
2	60	720	336	-
3	60	720	336	-
4	60	720	336	-
5	90	1080	504	-
6	120	1440	660	-
7	120	1440	390	-
8	120	1440	820	-
9	120	1440	147	824

Table 1 (continued)

Examples	Bath temperature (°C)		Conversion rate of C <sub>3</sub> H <sub>6</sub> (mol%)
	Tube 1	Tube 2	
1	340	250	92
2	340	250	88
3	325	260	94
4	330	270	95
5	325	271	92
6	342	255	94
7	330	256	89
8	340	272	95
9	335	272	92

Table 1 (continued)

Examples	Yield (mol%)		Space time yield/day per each tube (acrylic acid kg)	Concentration of acrylic acid in condensate (wt%)
	Acrylic acid	Acrolein as residue		
1	45	4	1.1	18-20
2	30/40	3	1.2/1.8	
3	55	1.6	2.2	
4	58	1.1	2.3	
5	56	1.1	3.4	
6	60	1.5	5.6	24.5
7	53	1.3	4.4	30
8	53	1.4	4.4	20.3
9	53	1.5	4.4	43.6

Examples 10 to 17:

Using a catalyst produced by known formulation, a mixture containing a fresh propylene, a fresh air and a circulated gas which was composed of 100 parts by volume of propylene, 252 parts by volume of oxygen, 50 parts by volume of water vapor and 1728 parts by volume of an inert gas (essentially composed of nitrogen containing a slight amount of carbon monoxide) which all were represented by total amounts per one hour, was passed through two reaction tubes connected in series with each other, and oxidized therein in a two-stage manner at temperatures shown in Table 2. The compositions of the respective catalysts used are also shown in Table 2. The catalyst used in the first reaction stage was constituted from 0.019 part by volume of a 25% activated component, 0.12 part by volume of a 50% activated component



and 0.91 part by volume of a 100% activated component which were disposed in a flow direction of the mixed gas, whereas the catalyst used in the second reaction stage was constituted from 0.019 part by volume of a 50% activated component and 0.73 part by volume of a 100% activated component which were also disposed in a flow direction of the mixed gas. The activity of the catalyst was reduced to a desired value by diluting with an inert material (steatite balls each having a diameter of 3 mm). The catalyst itself was used in the form of tablets each having a size of 3 x 3 mm. The circulated gas was such a gas obtained by substantially completely removing a condensable reaction product from the waste gas discharged from the second reaction stage by washing.

Contents of acrylic acid in the resultant condensates, acrylic acid yields, conversion rates of propylene and space time yields of acrylic acid are shown in Table 2.

Table 2

Examples	Catalyst	
	First reaction stage	Second reaction stage
10	$\text{Mo}_{10}\text{Ni}_{7.5}\text{Cr}_1\text{Fe}_{0.35}\text{Bi}_{0.83}\text{Sn}_{0.5}$ on 30 wt% $\text{SiO}_2$ (Example 1 of DOS 2000425)	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
11	$\text{Mo}_{10}\text{Ni}_{7.5}\text{Cr}_1\text{Fe}_{0.35}\text{Bi}_{0.83}\text{Sn}_{0.5}$ on 30 wt% $\text{SiO}_2$ (Example 1 of DOS 2000425)	$\text{Mo}_{12}\text{V}_{3.5}\text{Sb}_1$ on aluminum pellets (Example 1 of DOS 2038763)
12	$\text{Mo}_{10}\text{Ni}_{7.5}\text{Cr}_1\text{Fe}_{0.33}\text{Bi}_{0.83}\text{Ge}_1$ on 30 wt% $\text{SiO}_2$ (Example 6 of DOS 2000420)	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
13	$\text{Mo}_{10}\text{Ni}_{10}\text{Co}_{0.3}\text{Fe}_1\text{P}_1\text{Bi}_1$ + 1% $\text{Sm}_2\text{O}_3$ on 33 wt% aluminum silicate (Example 1 of Belgian Patent No. 738250)	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
14	$\text{Mo}_{12}\text{Ni}_1\text{Co}_3\text{Fe}_2\text{Bi}_1\text{P}_2\text{K}_{0.2}$ on 30 wt% $\text{SiO}_2$ (Example 1 of DOS 2020791)	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
15	$\text{Mo}_7\text{Ni}_{0.7}\text{Cr}_2\text{Te}_{0.35}$	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
16	$\text{Mo}_4\text{W}_8\text{Te}_{0.25}$ (British Patent No. 1243794)	$\text{Mo}_6\text{W}_1\text{V}_1\text{Fe}_{1.5}$ (Belgian Patent No. 746202)
17	$\text{Mo}_4\text{W}_8\text{Te}_{0.25}$ (British Patent No. 1243794)	$\text{Mo}_{12}\text{V}_{3.5}\text{Sb}_1$ on aluminum pellets (Example 1 of DOS 2038763)

Table 2 (continued)

Examples	Bath temperature (°C)		Concentration of acrylic acid in condensate (wt%)
	First stage	Second stage	
10	362	260	52
11	390	420	39
12	360	260	51
13	390	260	50
14	390	260	52
15	400	270	47
16	365	250	53
17	365	410	51

Table 2 (continued)

Examples	Conversion rate of $C_3H_6$ (mol%)	Yield of acrylic acid (mol%)	Space time yield/day per each tube (acrylic acid weight part)
10	91	52	4.0
11	76	39	3.0
12	94	53	4.1
13	79	50	3.9
14	62	44	3.4
15	79	38	2.9
16	94	54	4.2
17	90	52	4.0

Comparative experiment for Example 11:

The same procedure as defined in Examples 10 to 17 was

conducted using the same apparatus as used in Examples 10 to 17 except that 1.12 parts by volume of the 100% activated catalyst as described in Example 1 of the laid-open publication of German Patent No. 2000425 was used in the first reaction stage, and 0.91 part by volume of the 100% activated catalyst as described in Example 1 of the laid-open publication of German Patent No. 2038763 was used in the second reaction stage. A mixture composed of 100 parts by volume/hr of propylene, 1200 parts by volume/hr of air and 780 parts by volume/hr of water vapor was passed through the two reaction tubes connected in series with each other. The bath temperature for the tube 1 was set to 362°C, whereas the bath temperature for the tube 2 was set to 410°C. As a result, there were attained the conversion rate of propylene 92%, the space time yield of acrylic acid of 1.9 parts by weight/day per each tube, and the yield of acrylic acid of 25 mol% relative to propylene. The acrylic acid was produced only at a concentration of 14% by weight in the resultant condensate.

## AMENDMENT (VOLUNTARY)

February 18, 1972

Amendment (Japanese Patent Application No. 46-92013(1971))

The following amendment to the specification should be made.

1. Insert "in two stages" before "oxidized" appearing on page 2, line 8.

2. Amend "German Patent ..... 16 43 737.9" appearing on page 3, lines 11 to 12 to read as follows.

"Belgian Patent No. 705498 and Japanese Patent Application No. 44-1936(1969)"

3. Amend "German Patent ..... 19 08 965.7" appearing on page 4, lines 8 to 9 to read as follows.

" Japanese Patent Application Nos. 43-22935(1968) and 45-14864(1970)"

4. Insert ", bath temperature" after "gas amount" appearing on page 14, line 7.

5. Amend "(DOS 2000420, Example 6)" appearing on page 18, Table 2, the column of Example 12 to read as follows.

"(DOS 2000425, Example 6)"

6. Amend the description appearing on page 1, line 4 to the bottom line (entire sentence of the scope of the invention) to read as follow.

"2. SCOPE OF THE INVENTION:

1. A process for producing acrylic acid comprising a first reaction stage of oxidizing propylene into substantially acrolein in a reaction tube filled with a catalyst by using a mixed gas containing an inert diluting gas containing elementary oxygen and water vapor; and a second reaction stage of further oxidizing the acrolein into acrylic acid, wherein the propylene is oxidized under such a condition that an initial concentration of the propylene is more than 2 mol% based on a starting mixed gas, and at both the reaction stages, a space load in each reaction stage is controlled to more than 60 L/hr propylene per 1 L of the catalyst,

characterized in that an activity of the catalyst is changed through the two stages so as to increase up to 100% either continuously or stepwise from an inlet to an outlet of the reaction tube along the direction of the reaction tube, and a reaction waste gas from which a majority of a condensable gas obtained in an outlet of the second reaction stage is removed, is re-fed to the first reaction stage in place of a part or a whole of the water vapor as the inert diluting gas."



②特願昭 46-92013 ①特開昭 47-10614

④3 公開昭 47.(1972) 5.27

審査請求 無 (全 8 頁)

優先権主張  
ドイツ国/7741 11月18日

特許願 ( )

昭和 46 年 11 月 18 日

特許庁長官 井 土 武 久 殿

①9 日本国特許庁

## ⑬ 公開特許公報

### 1. 発明の名称

アクリル酸の製法

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明 細 書

### 1. 発明の名称

アクリル酸の製法

### 2. 特許請求の範囲

二段階において触媒の活性を変化させて、活性を反応管の入口から反応管の方向に絶えず又は階段的に 100% まで増大させ、そして第 2 反応段階の出口において得られる凝縮可能なガスを大部分除去した反応廃ガスを、不活性希釈ガスとしての水蒸気の一部又は全部の代わりに第 1 段階に再供給することを特徴とする、元素状酸素及び水蒸気含有不活性希釈ガスを含有する混合ガスを用い、触媒を装入した反応管中でプロピレンを本質的にアクロレインに酸化してアクリル酸とする第 1 段階及びアクロレインをさらに酸化してアクリル酸とする第 2 段階においてプロピレンを酸化し、この際プロピレンの初期濃度が出発混合ガスに対し 2 モル% を越え、そして両段階における空間負荷を各段階ごとに触媒 1 ㍑につき毎時プロピレン 60 ㍑より大きくすることによる、アクリル酸の製法。

### 3. 発明の詳細な説明

本発明は、酸化触媒を用いてプロピレンを、中間段階としてのアクロレインを経て二段階で酸化することによる、アクリル酸の製法に関する。

プロピレンを気相において酸素含有ガス及び水蒸気の存在下に、高められた温度において固体触媒上で酸化してアクリル酸とすることは公知である。この際プロピレンは第 1 段階において主としてアクロレインに酸化され、そして生成した混合ガスはアクロレインを分離することなく、第 2 段階における第 2 の触媒上でアクリル酸に酸化される。

この際第 1 段階のためには、周期律表第 IV a ~ VI a 族、第 VII 族ならびに第 IV b ~ VI b 族の元素を含有する触媒系が提案された。これらの触媒系の中でテルルを含有する触媒 (2 酸化テルルもしくはテルル酸を含有する触媒又はこの種の触媒であつてビスマス又はアンチモン、場合により銀を含有するもの) が、この反応に普通に用いられる硝石浴反応器の比較的低い浴温度

において、アクロレイン生成の特に高い選択性により優れている。この際モリブデン、タングステン及びテルルの酸化物又はコバルト、モリブデン及びテルルの酸化物を含有する触媒が考慮される。提案された他の触媒はたとえば鉄、錫、アンチモン及びバナジウム、あるいはニッケル、コバルト、鉄、ビスマス、燐及びモリブデンを酸素のほかにも含有し、場合により酸化サマリウム及び酸化タンタルが添加されている。プロピレンをアクロレインに酸化するための前記触媒系の製造及び使用についてはたとえばドイツ特許出願 P 15 42 030.1 及び P 16 43 737.9 号明細書に記載されている。

オ 2 段階のためには同様に前記の群から選ばれる酸化触媒が好ましいが、アクロレインをさらに酸化してできるだけ完全にアクリル酸に変えるため、一般に周期律表オ V a 族及びオ VI a 族の元素を用いず、特にセレン又はテルルは全く用いないか又はきわめて少量しか用いてはならないという制限を有する。公知の触媒はたとえばコバルト及びモリブデン又はモリブデン、

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ために必要な局部的に生成する反応熱の迅速な除去は、きわめて不経済な対策によりこの問題に立ち向う場合にのみ可能となる。たとえば狭い管断面を選ぶか又は低い温度、従つて低い触媒負荷及び管負荷（ガスの線速度）において操作し、さらに酸化すべきガスを多量（40 容量 % まで）の水蒸気を用いて希釈することにより、触媒上の爆発的燃焼又は少なくとも望ましくない副生物を生ずる過度の酸化から保護しなければならない。用いられたプロピレンに対し理論値の 50 % 以上となる、比較的良好なアクリル酸の絶対収率を得ることができる。しかしこの収率に達するためには、低い空間負荷（高い滞留時間）で操作することを要し、かつ生成したアクリル酸はきわめて希薄な水溶液として得られるにすぎないので、不経済な高いエネルギー費及び投資額を必要とする。

技術的な傾向は、これまで努力して得られた 1 回の導通において高い絶対収率を可能にする指針により、方法が全体として経済的となるように空時収量を高める方向に進んだ。本発明の

タングステン及びバナジウム、又は錫、アンチモン及びモリブデンを酸素のほかにも含有する。

有利には酸素のほかにもモリブデン、タングステンならびに鉄及び（又は）ニッケル及び（又は）マンガン及び（又は）銅及び場合によりバナジウムを含有する触媒が用いられる。この触媒の製造及びアクロレインをアクリル酸に酸化するための使用についてはドイツ特許出願 P 16 18 133.2 及び P 19 08 965.7 号明細書に記載されている。

前記文献の教えるところはすべて、最後に使用プロピレンに対する絶対収率ができるだけ高いアクリル酸に到達することを目ざしている。しかしこの方法を行なうために同様に重要な他の問題点は、十分な程度に考慮されてはいない。

最も重要な問題点は空時収量及び得られる凝縮物中のアクリル酸の濃度である。工業的装置においては実験に際して高い空時収量及び高い濃度を得るために著しい困難を生じた。気相酸化によるアクリル酸合成の工業的 1 段階又は多段階によれば、1 回の導通における高い変換率の

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目的は、前記のような過度の酸化を最低限度まで減少させ、かつ爆発的燃焼過程を確実に防止することのできる安全な酸化法を開発することであつた。

本発明者らは、二段階において触媒の活性を変化させて、活性を反応管の入口から出口まで絶えず又は階段的に 100 % まで増大させ、そしてオ 2 反応段階の出口において得られる凝縮可能なガスを大部分除去した反応廃ガスを、不活性希釈ガスとしての水蒸気の一部外又は全部の代わりにオ 1 反応段階に再供給することを特徴とする、元素状酸素及び水蒸気含有不活性希釈ガスを含有する混合ガスを用い、触媒を装入した反応管中でプロピレンを本質的にアクロレインに酸化するオ 1 段階及びアクロレインをさらに酸化してアクリル酸とするオ 2 段階においてプロピレンを酸化し、この際プロピレンの初期濃度が出発混合ガスに対し 2 モル % を越え、そして両段階における空間負荷を各段階ごとに触媒 1 g につき毎時プロピレン 60 g より大きくすることによるアクリル酸の製法により、前

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記目的が達成されることを見出した。

この方法によれば、生成するアクリル酸があまりに多量の水で希釈されて得られることを防止することができ、従つて純アクリル酸を得るための仕上処理にはきわめてわずかな時間及びエネルギーの消費を必要とするにすぎない。もちろんこの種の方法に対しては、技術上の先入見に従う限り、活性触媒物質の希釈により絶対収率が著しく低下すると考えられた。しかし予想外にもそうはならない。本発明方法によればこの種の系の本質的に高い空間負荷が可能となり、すなわち導通量を危険なく著しく高めることができ、この際本発明方法においては従来と同じく用いられたプロピレンに対し約50%の絶対収率が得られる。

触媒を希釈することのさらに他の利点は、合成用蒸気を公知のように水蒸気に比して著しく小さい熱容量を有する返送反応ガスに置き換えることにより、過度の酸化及び局部的過熱の危険を防止しうることである。これにより本発明方法の経済性は従来法に比して著しく改善され

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の半分以下の長さからのちに、触媒活性はすでに100%に達することが好ましい。希釈すべき部分における希釈の増加の程度はガスの線速度に依存する。ガスの線速度が高いほど、調節不可能な局部的温度上昇の発生を避けるため、反応管のはじめの部分において活性を著しく低下させなければならない。本発明によれば空の反応管につき60cm/秒を越えるガスの線速度において、希釈すべき層中の活性もしくは活性物質の割合が0から100%まで上昇することが好ましい。好ましくは活性物質の25~75%の希釈からはじめ、活性物質の割合を100%まで増大させる。希釈剤としては本反応において不活性であることを必要とし、少なくとも600℃、好ましくは700℃の温度まで熱安定性であり、できるだけ非多孔質の材料であつて、さらに反応条件下に触媒成分と化合物を形成しないものが用いられる。好適なものとはたとえば高温で処理されたアルミニウム、ジルコニウム、チタン、マグネシウム又は珪素の酸化物、その他高温で溶融する珪酸塩及びア

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ルモシリケート、電極黒鉛、セメント物質、高温で溶融する焼結材料、好ましくはステアタイト、α-アルミナ又は炭化珪素である。

希釈は好ましくは触媒成形物と、同一又はほとんど同一寸法の不活性材料からの成形物との混合によるか、又は微粉末とした触媒材料及び不活性材料を混合し続いて成形することにより行なわれる。

本発明方法は具体的には次のように行なわれる。まず出発混合物に対し2モル%を越えるプロピレン濃度を選び、そして毎時プロピレン60ℓを越える空間負荷において、特殊な触媒系とは無関係に80~85モル%を越えるプロピレンもしくはアクロレインの変化率のために必要な浴温を選ぶ。

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この混合ガスを反応させるため、活性触媒物質を不活性材料を用いて希釈し、触媒の活性が低下するようにする。この際希釈は、活性が反応管の入口から出口まで絶えず又は階段的に100%まで増加するように行なう。しかし反応管の末端より前ですでに100%に達するようにすることが好ましい。この際好ましくは触媒物質の全量に対し5~50重量%の触媒物質が本発明の手段により希釈される。この場合特に工業上興味あるものは活性触媒物質の10~30重量%の希釈である。言い換えれば、反応管

よりアクリル酸、水蒸気及び他の凝縮可能な生成物を除去された反応ガスは、第1反応段階に入る大部分がプロピレン、空気及び場合により水蒸気から成る出発混合ガスに添加混合され、混合の手段もしくは載は返送される戻ガス中の未反応のプロピレン及び酸素を考慮して、第1触媒層への入口の前のプロピレン濃度が全混合ガスに対し2モル%以上、好ましくは4~8モル%となり、そしてプロピレン：酸素：水のモル比が1：1.5~4：0~3、好ましくは1：2~3：0~2となるように定められる。

本発明方法において有利には、第1段階にお

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いてモリブデン、タングステン及びテルルを酸素のほか含有し、モリブデン：タングステンの原子比が0.03～40：1、好ましくは0.2～25：1であり、そしてテルル含量が0.2～2重量%、好ましくは0.5～1.8重量%である触媒が用いられ、オ1段階においてはモリブデン、タングステン及び鉄及び（又は）ニッケル及び（又は）マンガン及び（又は）銅を酸素のほか含有し、かつ場合によりバナジンを含有し、モリブデン：タングステン：鉄〔ニッケル、マンガン及び（又は）銅〕の原子比が1～20：0.01～10：1、好ましくは2～10：0.1～2：1、そしてモリブデン：バナジンの比が6：6～0.2、好ましくは6：0.5～4である触媒が用いられる。本方法のオ1及びオ2段階のためさらに好適なものは、プロビレンのアクロレインへの酸化もしくはアクロレインのアクリル酸への酸化のための他の普通の触媒、たとえばドイツ特許オ1924496号及びオ200425号各公開公報、ベルギー特許オ689720号、オ746202号及び英オ73825

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0号明細書、公開されたオランダ特許出願オ70.11603号及び特公昭45-22525号公報に記載のものである。

本発明方法によれば各段階ごとに毎時触媒1ℓ当たりプロビレン60ℓ以上、好ましくは100ℓ以上（ℓはいずれも標準状態）の高い管負荷及び空の反応管につき60cm/秒以上、好ましくは100cm/秒以上のガスの線速度において、80%以上特に85%以上の変化率ならびに用いられたプロビレンに対し45～50モル%のアクリル酸収率に相当する浴温度が可能となる。

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## 実施例1～9

下記実施例は、本発明方法により最初は著しく希釈された形で用いられ、次いで絶えず又は階段的に増加する濃度で用いられる触媒上に反応ガスを通す場合に、空時収量が希釈されない触媒を用いる場合よりも約2～3倍だけ高いことを示す。この方法における煙道ガスもしくはその一部分の再供給（実施例9）及びこれに結びつく水蒸気の置換はもはや空時収量を高めることはないが、これに反して得られる水溶液中のアクリル酸濃度を2倍に高める。

実験は詳細には次のように行なわれた。プロビレン（98%）、空気、水蒸気及び場合により1酸化炭素1.8容置%を含有する窒素からの混合物を、2個の直列に連結された長さ4m及び直径25mmの管から成る2段式装置に通す。管は電気的に加熱しうる、攪拌される塩浴中にある。管に入るガスはそれぞれの場合に熱交換器を経てほとんど塩浴の温度に予熱もしくは冷却される。オ2段階の200～300℃の熱い反応ガスは2段式急冷系中で、得られる凝縮物

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を用いて冷却される。オ1段階にはモリブデン-タングステン-テルル触媒、オ2段階にはモリブデン-タングステン-バナジン-鉄触媒が3×3mmの錠剤の形で装入されている。この装入物は入口層において直径3mmのステアタイト球を用いて希釈されている。

触媒量、希釈比、ガス量及びオ1段階に入るプロビレン（98%）の量に対して得られる変換率、アクリル酸収率、オ2段階後の残留アクロレン収率、空時収量ならびに得られるアクリル酸の凝縮物中の濃度を、オ1表に詳細に示す。

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オ 1 表

実施例	各管の触媒量 (ml)		ガス量 (ℓ/時)				浴 温 (°C)		C <sub>3</sub> H <sub>6</sub> 変化率 (モル%)	収 率 (モル%)		空 時 収 量 管 当 り 1 日 (アクリル酸kg)	凝縮物中のア クリル酸濃度 (重量%)
	管 1	管 2	C <sub>3</sub> H <sub>6</sub>	空 気	H <sub>2</sub> O	N <sub>2</sub> /CO	管 1	管 2		アクリル酸	アクロレ イン残り		
1	600 (活性物質 100 容量%)	300 (活性物質 100 容量%)	36	420	196	—	340	250	92	45	4	1.1	18~20
2	1000 ("100 容量%)	500 ("100 容量%)	60	720	336	—	340	250	88	30/40	3	1.2/1.8	
3	400 ("25 " " ) 900 ("100 " " )	500 ("100 " " )	60	720	336	—	325	260	94	55	1.6	2.2	
4	400 ("25 " " ) 900 ("100 " " )	400 ("25 " " ) 400 ("100 " " )	60	720	336	—	330	270	95	58	1.1	2.3	
5	400 ("25 " " ) 1100 ("100 " " )	400 ("25 " " ) 500 ("100 " " )	90	1080	504	—	325	271	92	56	1.1	3.4	
6	200 ("25 " " ) 150 ("33 " " ) 100 ("50 " " ) 1050 ("100 " " )	400 ("25 " " ) 700 ("100 " " )	120	1440	660	—	342	255	94	60	1.5	5.6	24.5
7	"	"	120	1440	390	—	330	256	89	53	1.3	4.4	30
8	120 ("25 " " ) 210 ("33 " " ) 140 ("50 " " ) 1030 ("100 " " )	120 ("25 " " ) 210 ("33 " " ) 140 ("50 " " ) 630 ("100 " " )	120	1440	820	—	340	272	95	53	1.4	4.4	203
9	"	"	120	1440	147	824	335	272	92	53	1.5	4.4	43.6

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## 実施例 10 ~ 17

公知の処方により製造された触媒の使用下に、毎時合計でプロピレン 100 容量部、酸素 25 2 容量部、水蒸気 50 容量部及び不活性ガス（少量の 1 酸化炭素のほか本質的に窒素）172 8 容量部から成る、新しいプロピレン、新しい空気及び循環ガスからの混合物を、直列に配置された 2 個の反応管中で、オ 2 表に示す温度において 2 段階に酸化する。触媒の組成はオ 2 表に示す。オ 1 段の触媒は混合ガスの流れの方法に活性の 0.091 容量部、50% 活性の 0.12 容量部及び 100% 活性の 0.91 容量部から構成され、オ 2 段の触媒は 50% 活性の 0.091 容量部及び 100% 活性の 0.73 容量部から構成される。触媒の活性は不活性物質（直径 3 mm のステアタイト球）を用いて希釈することにより所望の値に減少させる。触媒自体は 3 × 3 mm の錠剤として用いられる。循環ガスはオ 2 段階の腐ガスから凝縮可能な反応生成物を實際上完全に洗浄除去したものである。

凝縮物中のアクリル酸の割合、アクリル酸収率、プロピレンの変化率及びアクリル酸の空時収量をオ 2 表に示す。

オ 2 表

実施例	触 媒	浴温 (°C)		凝縮物中の アクリル酸 (重量%)	C <sub>3</sub> H <sub>6</sub> 変化率 (モル%)	アクリル酸 収 率 (モル%)	空時収量 毎当り1日 (アクリル酸重量部)
		1段	2段				
10	オ 1 段 30重量%のSiO <sub>2</sub> 上 Mo <sub>10</sub> Ni <sub>15</sub> Cr <sub>1</sub> Fe <sub>0.5</sub> Bi <sub>0.5</sub> Sn <sub>0.5</sub> (DOS 2000425, 実施例1)	オ 2 段 Mo <sub>8</sub> W <sub>1</sub> V <sub>1</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	362 260	52	91	52	4.0
11	"	A1ペレット上 Mo <sub>12</sub> V <sub>3.8</sub> Bi <sub>1</sub> (DOS 2038763 実施例1)	390 420	39	76	39	3.0
12	30重量%のSiO <sub>2</sub> 上 Mo <sub>10</sub> Ni <sub>15</sub> Cr <sub>1</sub> Fe <sub>0.5</sub> Ge <sub>1</sub> (DOS 2000420, 実施例6)	Mo <sub>8</sub> W <sub>1</sub> V <sub>1</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	360 260	51	94	53	4.1
13	33%の珪酸アルミニウム上 Mo <sub>10</sub> Ni <sub>10</sub> Co <sub>0.5</sub> Fe <sub>1</sub> P <sub>1</sub> Bi <sub>1</sub> +1%Sm <sub>2</sub> O <sub>3</sub> (ベルギー特許オ738250号, 実施例1)	Mo <sub>8</sub> W <sub>1</sub> V <sub>1</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	390 260	50	79	50	3.9
14	30%のSiO <sub>2</sub> 上 Mo <sub>12</sub> Ni <sub>1</sub> Co <sub>3</sub> Fe <sub>2</sub> Bi <sub>1</sub> P <sub>2</sub> K <sub>0.2</sub> (DOS2020791, 実施例1)	Mo <sub>8</sub> W <sub>1</sub> V <sub>1</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	390 260	52	62	44	3.4
15	Mo <sub>7</sub> Ni <sub>0.7</sub> Cr <sub>2</sub> Te <sub>0.5</sub>	Mo <sub>8</sub> W <sub>1</sub> V <sub>1</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	400 270	47	79	38	2.9
— 18 —							
16	Mo <sub>4</sub> W <sub>8</sub> Te <sub>0.25</sub> (英国特許オ1243794号)	Mo <sub>8</sub> W <sub>1</sub> V <sub>1.5</sub> Fe <sub>1.5</sub> (ベルギー特許 オ746202号)	365 250	53	94	54	4.2
17	"	A1ペレット上 Mo <sub>12</sub> V <sub>3.8</sub> Bi <sub>1</sub> (DOS 2038763 実施例1)	365 410	51	90	52	4.0

## 実施例 11 に対する比較実験

実施例 10～17 と同じ装置で操作し、ただしオ 1 段にはドイツ特許オ 200,0425 号公開公報実施例 1 に記載の 100 ㉿活性触媒 1・12 容量部を用い、オ 2 段階にはドイツ特許オ 2038763 号公開公報実施例 1 に記載の 100 ㉿活性触媒 0.91 容量部を用いた。2 個の直列に配置された反応管に、毎時プロピレン 100 容量部、空気 1200 容量部及び水蒸気 780 容量部からの混合物を通す。管 1 のための浴温は 362℃、管 2 のための浴温は 410℃である。92 モル㉿のプロピレン変化率、管当たり 1 日にアクリル酸 1・9 重量部の空時収量及び用いられたプロピレンに対し 25 モル㉿のアクリル酸収率が得られる。アクリル酸は凝縮物中に 14 重量㉿の濃度で得られるにすぎない。

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## 手 続 補 正 書 (自 発)

昭和 47 年 2 月 18 日

特許庁 長 官 井 土 武 久 殿

## 1. 事件の表示

特願昭 46-92013 号

## 2. 発明の名称

アン セイホク  
アクリル酸の製法

## 3. 補正をする者

事件との関係 特許出願人

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電話 (591) 0914 番

## 5. 補正命令の日付

昭和 年 月 日

## 6. 補正により増加する発明の数

## 7. 補正の対象 明細書の特許請求の範囲及び発明の

## 8. 補正の内容 詳細な説明の項

別紙訂正書のとおり

## 6. 前記以外の発明者

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本出願については下記特許出願による優先権を主張します。

出 願 国 ドイツ国

出 願 日 西暦 1970 年 11 月 18 日

出 願 番号 P 20 56 6147

## 訂 正 書 (特願昭 46-92013 号)

明細書中下記の訂正を行なう。

- オ 2 頁 8 行の『酸化して』の前に『2 段階で』を加入する。
- オ 3 頁 11～12 行の『ドイツ特許…… 16 4 3 737.9 号』を下記のとおり改める。  
『ベルギー特許オ 705498 号及び特願昭 44-1936 号』
- オ 4 頁 8～9 行の『ドイツ特許…… 19 08 965.7 号』を下記のとおり改める。  
『特願昭 43-22935 号及び同 45-148 64 号』
- オ 14 頁 7 行の『ガス量』の後に『、浴温』を加入する。
- オ 18 頁のオ 2 表において、実施例 1.2 の欄の『( DOS 2000420、実施例 6 )』を下記のとおり改める。  
『( DOS 2000425、実施例 6 )』

6. 第1頁4～終行（特許請求の範囲の項の全文）  
を次のとおり改める。

【2. 特許請求の範囲】

二段階において触媒の活性を変化させて、活性を反応管の入口から出口まで反応管の方向に絶えず又は階段的に100%まで増大させ、そして第2反応段階の出口において得られる凝縮可能なガスを大部分除去した反応廃ガスを、不活性希釈ガスとしての水蒸気の一部又は全部の代わりに第1段階に再供給することを特徴とする、元素状酸素及び水蒸気含有不活性希釈ガスを含有する混合ガスを用い、触媒を装した反応管中でプロピレンを本質的にアクロレインに酸化する第1段階及びアクロレインをさらに酸化してアクリル酸とする第2段階においてプロピレンを酸化し、この際プロピレンの初期濃度が出発混合ガスに対し2モル%を越え、そして両段階における空間負荷を各段階ごとに触媒1gにつき毎時プロピレン60gより大きくすることによる、アクリル酸の製法。』

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優先権証明書訳文

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・アクチエンゲゼルシャフト(6700 ルードウィツヒスハーフ  
エン所在)は下記の名称の発明について、

アクリル酸の製法

西暦 1970 年 11 月 18 日にドイツ国特許庁に特許  
出願した。

ここに添付の書類はこの特許出願の出願時におけるものの  
真正な謄本である。

西暦 1971 年 10 月 8 日

ドイツ国特許庁長官代理  
署 名

出願番号 P 20 56 614.7